COPOLYMERIZATION OF HETEROCYCLIC MONOMERS BY RING SCISSION

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INTRODUCTION

Homopolymerization processes utilizing cyclic monomers such as ω - caprolactam and the alkene oxides have been studied extensively in academic laboratories and in industry. Indeed, reactions of this type are the basis for some of the useful polymers produced in this country. The preparation of nylon-6 from ω - caprolactam is an outstanding example of this type of reaction. Although several steps are involved in the preparation of this monomer its use continues to increase (65). The capacity of the chemical industry in this country for production of nylon-6 in 1962 is an estimated 152 million pounds (65). Other well-developed industrial processes in this area include the homopolymerization of alkene oxides and oxetanes.

In contrast, however, only a few copolymers have been prepared from cyclic monomers. Synthetic polypeptides containing two or more amino-acid residues have been prepared from the 4-substituted-2,5-oxazolidinediones (N-carboxy amino acid anhydrides, or NCA's), but these compounds are used principally as model compounds for protein studies (13), and, in spite of a group of patent claims, have not been found to give inexpensive, useful products attractive to industry. Of the few studies of copolymerization in this area, only a very small number have been concerned with the kinetics of ring-scission copolymerization.

This investigation had two main objectives. The first of these was to prepare novel copolymers from monomers which are known to homopolymerize by ring scission. Properties such as softening point,

solubility, intrinsic viscosity, and molecular weight were to be determined. Also, the classical copolymer equation derived for radical copolymerization was to be tested to determine if the process obeyed this theory.

The second objective in the investigation was to determine if the Katchalski-Shalitin theory (162), recently proposed and tested for 2,5-oxazolidinediones, was applicable to other cyclic monomers which undergo ring-scission copolymerization.

HISTORICAL

Carothers (35) classified polymerization reactions as either addition or condensation processes. Polymerizations of cyclic monomers cannot be placed in either category, but in some respects are similar to both. Flory (69) and Priest (153a) suggest that polymers prepared from cyclic monomers should be considered condensation polymers since the monomer itself is a condensation product of one or more bi-functional compounds; and, as such, the resulting linear polymer can be considered a polymeric derivative of the bi-functional monomer.

On the other hand, in addition polymerization (35) the molecular formula of the repeating unit of the polymer chain is identical to that of the monomer, whereas in condensation polymerization the polymer is formed from monomer units with the elimination of a small molecule such as H_2O. The polymerization of alkene oxides and most cyclic monomers is thus an addition process. The NCA's polymerize with loss of CO_2, but this is not the result of an intermolecular reaction as is the case in typical condensation polymerization.

In addition polymerization, growing polymer reacts only with monomer, whereas in condensation polymerization any two molecular species may react. Cyclic monomers polymerize only by reaction of monomer with growing polymer (26).

In addition polymerization (26) high polymer is formed early in the reaction, and although increased reaction times result in better yields the average molecular weight remains approximately constant.

In contrast, in condensation polymerization (26) the average molecular weight increases with time. This occurs with cyclic monomers also, although then average molecular weights are determined largely by mole ratio of monomer to initiator (69).

Küchler (123) classifies as addition any polymerization process for which the activation energy of initiation is much greater than that of propagation. This results in a very low concentration of growing polymer; it has been estimated (26) that only approximately 10^{-8} parts of growing chain are present. In condensation polymerization the initiation and propagation steps are similar and the energies of activation should also be similar. For cyclic monomers also (69), the initiation and propagation steps are similar and should proceed at comparable rates. These are apparently not chain reactions (69) although under certain conditions this is probably not entirely true (156).

In polymerization reactions if the growth of polymer molecules proceeds in such a manner that equal opportunities are afforded for all, the resulting molecular weight distribution will be extremely narrow (69). Such a situation prevails if the rates of initiation and propagation are approximately the same. Flory (69) points out that such a distribution is much narrower than could be obtained by polymer fractionation. Three conditions are necessary for this narrow distribution. First, growth of polymer must proceed entirely by addition of monomer to the reactive end group of the growing polymer. Second, all reactive end groups must be equally available for reaction with monomer and this condition must prevail throughout the reaction. Third, all active centers must be introduced at the beginning of the reaction so that all molecules will have a similar growth period, and chain transfer or

termination must not occur since either of these processes would alter the molecular weight distribution. These conditions seem to apply to polymerizations of NCA's (66, 171) and some other cyclic monomers (69), but not to classical addition or condensation processes.

Although these characteristics are descriptive of homopolymers, some are probably equally true for copolymers prepared from cyclic monomers.

Hall and Schneider (96) investigated the polymerizability of cyclic monomers of various ring size. They found that lactones, urethanes, imides, anhydrides, ureas, and lactams containing 4, 7, or 8 atoms in the ring nearly always polymerize. Substituents on the ring usually decrease the polymerizability. Rings containing 5 or 6 atoms may or may not polymerize, depending on the class of the compound.

In the present investigation, experiments were confined to small ring monomers or at least to polymers with 3- or 4-atom repeating units.

CYCLIC MONOMERS USED

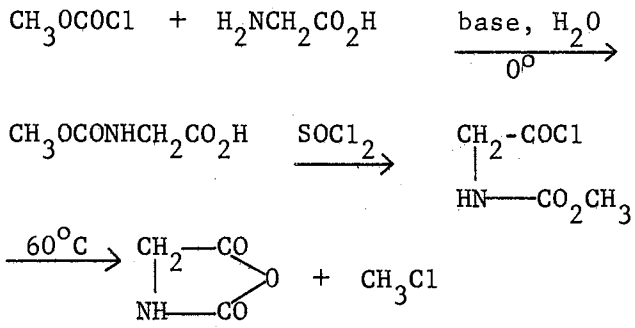
NCA's

The 4-substituted-2,5-oxazolidinediones are also known as N-carboxy-α-amino acid anhydrides, as Leuchs anhydrides, and simply as NCA's. These compounds are crystalline solids which have sharp melting points when pure (13). Several excellent reviews on the chemistry of NCA's have been published (13, 118, 119).

Synthesis of NCA's. NCA's have been prepared by four methods (13), three of which may be described as general procedures.

A. Leuchs Synthesis. The NCA's were discovered by Leuchs in

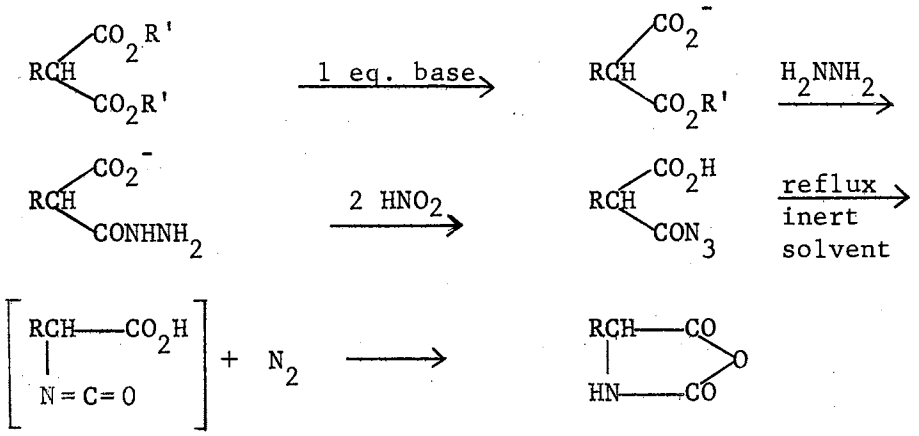
1906 (125). He found that the methyl carbamate derivative obtained from the reaction of an α-amino acid with methyl chloroformate in cold, aqueous alkaline solution at 0° C gave an unstable acid chloride upon treatment with thionyl chloride. When heated to 60° C the acid chloride underwent an intramolecular nucleophilic displacement (to use modern language) resulting in ring-closure and evolution of methyl chloride. Using glycine as the amino acid the over-all reaction may be illustrated by the following equation:



The methyl carbamate derivatives formed by treatment of the amino acid with methyl chloroformate are often oils which are difficult to purify (13). Bergmann and Zervas (18) found the benzyl carbamate derivatives much easier to isolate and purify. Another modification of the Leuchs synthesis was recently proposed by Katchalski and Ben-Ishai (16). The acid bromide apparently cyclizes much more readily than the acid chloride; that is, bromide ion is a better leaving group in the nucleophilic displacement than is chloride ion.

B. Curtius Synthesis. The Curtius method (41, 42) is not often used because it involves several steps. Yet it has the important advantage that the NCA can be prepared without using an amino acid as starting material. The most important step in this synthesis is apparently a very interesting and unusual example of the well known Curtius

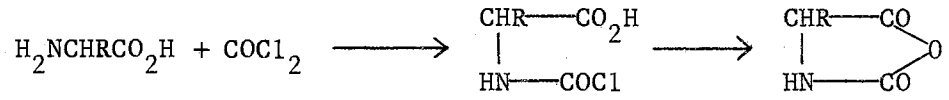
rearrangement (165). The starting material used in this procedure is a monosubstituted dialkyl malonate. The diester is first saponified to a monoester, which upon treatment with hydrazine gives the half-acid acyl azide by oxidation with nitrous acid. In the Curtius rearrangement if the acyl azide is refluxed in an inert solvent, the azide loses nitrogen gas and rearranges to an isocyanate (165). Curtius found that when the half-acid acyl azide was decomposed in inert solvent, the product obtained was an NCA. The NCA is apparently obtained by first a Curtius rearrangement to the isocyanate, followed by an intramolecular reaction with the carboxyl group to effect ring closure. The over-all process is illustrated by the following equation:



A similar synthesis based on the Lossen rearrangement was reported (105), but neither the NCA nor the isocyanate was isolated although polypeptide and CO_2 were obtained.

C. Fuchs Synthesis. Fuchs (74) prepared the NCA of N-phenylglycine by reacting the amino acid with phosgene in cold, aqueous alkaline solution. Normally this procedure cannot be used without modification because of the sensitivity of most NCA's to water and alkali (13). Several workers have found that the use of dry, inert solvents such as dioxane, toluene, or tetrahydrofuran makes possible the synthesis of the more reactive NCA's by this method (7, 61, 127).

This is the easiest of the three methods; it has therefore been most patented, and its use is recommended whenever possible. Extreme caution should be exercised because of the toxicity of phosgene. The reaction involves first the formation of a carbamyl chloride (64) which during work-up of the product undergoes ring closure with the evolution of HCl. The over-all synthesis is illustrated by the following equation:



Protection of Reactive Functional Groups. The NCA's are sensitive to many types of compounds including alcohols, amines, and acids. If hydroxyl groups or extra amino or carboxyl groups are present in the amino acid, these groups must be protected before the NCA is prepared (13).

Extra amino groups are usually protected by the use of benzyl chloroformate (19). The protective carbobenzoxy group may be removed by reduction with phosphonium iodide (100) or by anhydrous HBr in glacial acetic acid (15).

Carboxyl groups are usually protected by preparing the methyl ester (37, 97, 99) or the benzyl ester (17, 70, 90). These groups may be removed, after the NCA has been polymerized, by alkaline hydrolysis in aqueous-alcoholic solution (87, 99), or in the case of the benzyl ester, by reduction with phosphonium iodide (70) or with sodium in liquid ammonia (99).

Hydroxyl groups are protected by esterification with acetic anhydride in $HClO_4$ or benzyl chloroformate. After polymerization these groups may be removed by treatment with concentrated aqueous ammonia at room temperature without appreciable degradation of the polymer

"backbone" (71, 72).

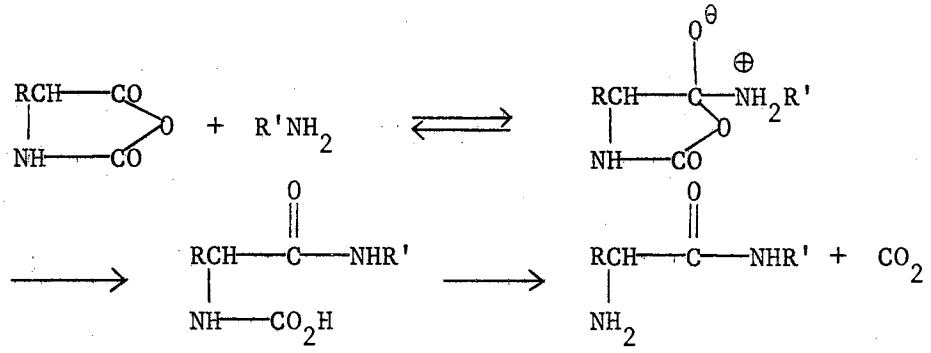
Polymerization of Monomers. NCA's have been polymerized in bulk by H_2O or H_2O vapor (84, 126, 138, 177, 178), in the liquid state (120, 126), and in solution (13, 119).

Woodward and Schramm (180) copolymerized a pair of NCA's in reagent benzene using the H_2O present as initiator. After two weeks a copolymer was obtained which had an intrinsic viscosity of ten. This corresponds to a molecular weight of several million. Another group (29) prepared a similar copolymer, but reported a molecular weight of only 15,000 determined by end-group analysis. The experimental data of Woodward and Schramm (180) were confirmed (55) by further experimentation, but it was shown that the viscosity decreased and the osmotic pressure increased at elevated temperatures or upon addition of a small amount of formic acid. Addition of 2 per cent of formic acid caused a one-hundred fold drop in intrinsic viscosity, and addition of more acid had no further effect. These findings indicate that the copolymer is highly associated in benzene, and that the association is partly overcome at elevated temperatures or in the presence of polar substances (55).

Primary (106, 129), secondary (161), and tertiary amines (150, 163) as well as preformed polypeptides (8, 98, 171, 172) have also been used as initiators for polymerization of NCA's. Alkoxides (107) and apparently Lewis bases in general also serve as initiators.

Several mechanisms (10, 27, 107, 171) have been proposed for the polymerization of NCA's. This subject was recently reviewed by Goodman (86).

One of these mechanisms, designated as the carbonyl addition mechanism (29), is shown below:



The propagation step is simply addition of the terminal amino group to another NCA molecule as in the initiation step. A possible termination step (161) involves reaction of the amino group with the other carbonyl of an NCA. If this reaction occurs, both end groups are carboxyl groups.

A recent review (12) calls attention to the fact that often polymerization of NCA's is a very complex process. Ballard and Bamford (9) have observed that if polysarcosine of degree of polymerization about ten is used as initiator for NCA's having unsubstituted NH groups, the polymerization is much faster than would be expected, and very much faster than ordinary secondary base-initiated polymerization (12). Poly-N-ethyl- and poly-N-benzylglycine as initiators also show this effect (12). This is described as a "chain effect" (9) and is said to be caused by polymerization of the NCA on the surface of the initiator.

Also when sarcosine-NCA is polymerized in benzene, the rate increases markedly after the polymer precipitates (11), but the same monomer does not show this increased rate when polymerized homogeneously in nitrobenzene (12). Ballard and Bamford (12) suggest that the polymer-rich phase is a better solvent for the NCA than the original medium, and since this phase also contains reactive terminal amino groups an increase in reaction rate is observed.

Still others (49, 106, 129) have reported that the rate of reaction

of NCA's increases when the growing chain attains an average size of seven to twelve units. Mitchell, Woodward and Doty (142) suggest that if the polypeptide contains ten units a significant portion of α-helix is present, and that the rate increase at this stage results from a change in configuration of the growing chain from random coil to α-helix. Weingarten (175) proposed a possible mechanism in which the NCA is hydrogen-bonded to the end of the α-helix near the terminal amino group.

Apparently the NCA's do not undergo a change in steric configuration when polymerized (97, 118, 120) since racemization is not observed.

Many copolymers (119) of NCA's have been prepared, and recently (162) a theory of copolymerization was proposed and experimentally verified.

Mention should also be made of analogs of NCA's. Treatment of α-hydroxy or α-mercapto acids with phosgene gives the corresponding 1,3-dioxolan-2,5-dione or thio derivative (43, 158b).

β-Lactones

The chemistry of β-lactones has been reviewed by Zaugg (183). More recently the reactions of β-propiolactone, including polymerization, were reviewed by Machell (130).

The first β-lactone isolated was reported by Einhorn (54) in 1883. Erlenmeyer (58) had earlier attempted to prepare β-phenyl-β-propiolactone, but failed and concluded that the compound was too unstable to isolate.

Preparation of Monomers. Only two general methods (183) are available for the preparation of β-lactones. These are: (a) the reaction of

a β-halo acid with a base, and (b) the reaction of ketenes with carbonyl compounds.

β-Propiolactone was first prepared by Johansson (114) from β-iodopropionic acid and silver nitrate. The preparation of β-lactones by this procedure is a stereospecific reaction (25, 115, 112) since optically active β-lactones are formed from optically active β-halo acids. (-) Iodosuccinic acid gives the optically active β-lactone of malic acid (104).

The preparation of β-lactones from ketenes and carbonyl compounds was reviewed by Hagemeyer (95). This reaction requires a catalyst unless the ketene component is diphenylketene (183). The better catalysts (95) include boric acid, triacetyl borate, mercuric chloride, zinc chloride, zinc thiocyanate, magnesium perchlorate, and boron trifluoride etherate.

β-Propiolactone is a highly reactive compound which may undergo acyl- or alkyl-oxygen cleavage when exposed to a given reagent (183). In general, if the reagent reacts in the ionized form alkyl-oxygen cleavage predominates (183) as has been observed (183) with strong mineral acids, salts of phenols and thiophenols, and salts of organic (91) and inorganic acids (92). Acyl-oxygen cleavage results with acid chlorides and anhydrides, thionyl chloride, and phosphorus pentachloride (183).

In neutral solution hydrolysis involves cleavage of the alkyl-oxygen bond, but in strongly acid or basic solution acyl-oxygen cleavage predominates for β-butyrolactone (147, 148), as well as for β-propiolactone (128).

In the presence of a basic catalyst β-propiolactone reacts with

alcohols largely with acyl-oxygen cleavage; if no catalyst or an acid catalyst is used the lactone undergoes alkyl-oxygen cleavage (94). With primary and secondary amines β-propiolactone may give products resulting from either acyl- or alkyl-oxygen cleavage depending upon conditions (93, 111).

Polymerization of Monomers. β-Propiolactone polymerizes on heating (89, 90, 96) to 150° for several hours. Many catalysts have been used to polymerize the lactone. The most effective catalysts (89, 90) are ferric chloride, stannic chloride, sulfuric acid (112), and sodium hydroxide. Sodium acetate (88, 91), potassium carbonate (183), potassium carbonate-copper acetate (113), alkali metals (109), and the metal alkyls of zinc, cadmium, and aluminum (109) have also been used.

The polymer is a polyester-acid, usually of low molecular weight, which has carboxyl and either hydroxyl or vinyl end groups (90). A typical polymer (90) had an average molecular weight of 1,000, melted at 86°, was soluble in hot acetone, and contained more vinyl than hydroxyl end groups. This polymer could be hydrolyzed to hydracrylic acid, alcoholyzed to ethyl hydracrylate, and pyrolyzed to acrylic acid.

β-Butyrolactone has been polymerized by heating (96), and with potassium carbonate (183), potassium carbonate-copper acetate (113), and diethylzinc (109) catalysts.

A recent patent (121) claims substituted β-lactones can be polymerized with tertiary amines to give film-forming materials of molecular weight of 5,000 to 10,000.

Enol-Lactones

Enol-lactones react differently than saturated lactones. These

compounds can be polymerized with suitable catalysts (101).

Preparation of the β-Lactone of 2,2,4-Trimethyl-3-hydroxy-3-pentenoic Acid (101). Tetramethyl-1,3-cyclobutanedione rearranges to the β-lactone of 2,2,4-trimethyl-3-hydroxy-3-pentenoic acid (TMBL) in the presence of a trace of anhydrous $AlCl_3$.

Polymerization of the β-Lactone of 2,2,4-Trimethyl-3-hydroxy-3-pentenoic Acid (101). TMBL in ether solution is polymerized by sodium methoxide to a polyester of 2,2,4-trimethyl-3-hydroxy-3-pentenoic acid. The molecular weight of the polymer was reported to be 11,900.

Alkene Oxides

Ethylene oxide, the parent member of this series, was discovered by Wurtz (181) in 1859. Berthelot (21) had previously prepared epichlorohydrin, but did not understand the nature of the reaction between the base and the halohydrin which he used. Propylene oxide was first prepared by Oser (149) in 1861.

Preparation of Monomers. Ethylene oxide is produced industrially by two methods, only one of which is applicable to other members of the series (85, 160). The first of these is the dehydrochlorination of ethylene chlorohydrin with alkali, and the other is the direct oxidation of ethylene with air or oxygen using a silver catalyst. Claims have been made for the preparation of propylene oxide by the latter process, but the major product is acrolein (85). Oxidation therefore occurs largely at the allylic position. The dehydrohalogenation reaction is more general since propylene oxide and other members of the series can be prepared by this procedure (85, 103).

The preparation, properties, and reactions of alkene oxides have

been reviewed by Goldstein (85) and by Curme and Johnston (40, 103, 160).

Polymerization of Monomers. The preparation, structure, and properties of polyethylene glycols and polypropylene glycols have been reviewed (40, 51, 103). Polyethylene glycols range from water-white liquids to wax-like solids, and are used as lubricants, solvents, vehicles, binders, and as intermediates in the rubber, food, pharmaceutical, cosmetic, agricultural, textile, paper, petroleum, and other industries (40).

Wurtz observed that ethylene oxide polymerizes to a wax-like solid in the presence of $ZnCl_2$ or a trace of alkali (182). In the presence of base, ethylene oxide reacts with preformed polyethylene glycol to give polymers of even higher molecular weight (151). The polymerization is catalyzed by both Lewis acids and bases (166).

The kinetics of the alkali metal alkoxide-initiated homopolymerization of ethylene oxide has been studied recently (50, 82). With dioxane as solvent it was necessary to add the alcohol of the corresponding alkoxide initiator to dissolve the base (82). The catalyst was sufficiently soluble in tetrahydrofuran that no dilution was necessary (50). The proposed (82) initiation and propagation steps for the sodium alkoxide-initiated homopolymerization reactions are:

$$RO^-(Na^+) + C_2H_4O \longrightarrow ROC_2H_4O^-(Na^+)$$

and

$$R(OC_2H_4)_nO^-(Na^+) + C_2H_4O \longrightarrow R(OC_2H_4)_{n+1}O^-(Na^+)$$

This seems to be another example of a polymerization reaction without termination (82).

The cationic polymerization of ethylene oxide has been studied and found to be very complex (124a, 137b, 180a, 180b). The molecular weight proceeds only to about 700 with BF_3 etherate catalyst. If high molecular weight polyethylene glycol is added to the reaction mixture, the polymer is depolymerized to molecular weight 700, and this reduction of molecular weight is accompanied by formation of dioxane. When the molecular weight reaches 700, the rate of depolymerization apparently is equal to the rate of polymerization. Depolymerization occurs at the ether linkages of the polymer molecule by a chain reaction caused by oxonium ions. The polymerization, however, appears to occur through a stepwise addition of monomer to terminal hydroxyl of the polymer molecule.

Bailey and France (6) recently copolymerized ethylene oxide and a number of other alkene oxides with basic catalysts including calcium amide and the calcium salt of ethylene glycol. A single relative copolymerization rate was determined for each pair. This relative rate is the alpha value of Wall's (173) copolymer composition equation.

Murbach and Adicoff (143) polymerized tetrahydrofuran and ethylene oxide with boron trifluoride etherate, and concluded from the monomer reactivity ratios which they determined that if the terminal unit of the copolymer was derived from ethylene oxide, this unit added a tetrahydrofuran molecule about twelve and one-half times as often as it did another ethylene oxide monomer. If the terminal unit was derived from tetrahydrofuran it showed a preference for monomers of its own type over those of ethylene oxide. The numerical values obtained for monomer reactivity ratios of ethylene oxide and tetrahydrofuran respectively were 0.08 and 2.2.

Propylene oxide and epichlorohydrin have also been copolymerized and the monomer reactivity ratios have been determined (110). The r value for epichlorohydrin is 1.8 ± 0.3 and for propylene oxide is 0.6 ± 0.5.

In recent years much of the research in epoxide chemistry has been concerned with the development of catalysts which produce crystalline polymers. Stereoregular polymerization has been reviewed by Gaylord and Mark (80) and by Eliel (57).

Alkenimines

Three-membered heterocyclic rings containing one nitrogen atom are known as aziridines and also as ethylenimines. These compounds may be considered the nitrogen analogs of alkene oxides (4). The parent compound of this series is extremely toxic (4). Its basic strength is somewhat less than that of ammonia and secondary aliphatic amines (30). The chemistry of aziridines was recently reviewed (4, 22).

Preparation of Monomers. Ethylenimine was first prepared by Gabriel (78, 79) from β-bromoethylammonium bromide and potassium hydroxide; its structure was established as cyclic by Marckwald (131). Substituted ethylenimines have also been prepared by this procedure (102, 179).

The inner salt, $H_3\overset{+}{N}CH_2CH_2OSO_3^-$, prepared from ethanolamine and sulfuric acid, loses the elements of sulfuric acid when distilled from base and undergoes ring-closure to ethylenimine. This reaction is known as the Wenker synthesis (176), and has been used to prepare homologs of ethylenimine (115). Modifications of the reaction have been developed (4, 56), one of which increases the yield to 70-80 per cent (56).

An interesting synthesis of the D- and L-isomers of propylenimine utilized the Wenker synthesis as the last step of a three-step procedure (141, 153). D- and L-alanine were converted to corresponding esters and then reduced to the amino-alcohols with $LiAlH_4$. When subjected to the Wenker reaction, the amino-alcohols gave the optically active D- and L-2-methylaziridines.

Another general procedure for the preparation of aziridines is the reaction of ketoximes with Grignard reagents (32).

Other procedures (36, 124) have been developed for the preparation of specific alkenimines.

Polymerization of Monomers. Ethylenimine is stable at room temperature and at elevated temperatures in the absence of acid. If heated under CO_2-free air or N_2, only a negligible amount of polymerization occurs. Polymerization cannot be initiated by peroxides or by ultraviolet light, nor by basic compounds (22).

Strong Lewis and mineral acids are the most effective catalysts for the polymerization of alkenimines (141). Among the better catalysts are BF_3, HCl, and anhydrous $FeCl_3$ (153). Carbonic acid also polymerizes the aziridines (22, 102). Alkenimines have been observed to polymerize explosively with BF_3-acetic acid catalyst (22). Other catalysts which have been used include diazonium salts (24) and oxonium, ammonium, and sulfonium salts (23).

The mechanism of the acid-catalyzed polymerization of ethylenimine and N-substituted imines has been studied (13a, 13b). The polymerization of ethylenimine consists of a stepwise reaction of iminium ions with uncharged imine.

The kinetics of the reaction are very complex. The rate rapidly

decreases during the early stage of the reaction. Extraneous amine reduces the rate only slightly. Barb (13a) thus rejects the idea that the polymer reduces the concentration of catalyst available to the monomer, and attributes the decrease in rate to destruction of the catalyst by reaction with the monomer.

The polyethylenimines are usually low molecular weight sirups or solids (116, 141, 153). Both the D- and L-isomers of propylenimine polymerize to optically active solid polymers, but the DL-isomer gave only a liquid polymer (141, 153).

3,3-bis(Halomethyl)oxetanes

The intramolecular ethers of pentaerythritol are 3,3-disubstituted oxetanes and 2,6-dioxaspiro[3.3]heptane (20). The four-membered heterocyclic ring is known as trimethylene oxide, oxetane, and oxacyclobutane. The chemistry of the oxetanes was recently reviewed (20, 132).

Preparation of Monomer. The 3,3-bis(halomethyl)oxetanes are prepared by the dehydrohalogenation of 2,2,2-tris(halomethyl)ethanol or the acetate derivative (20). The yields of monomer obtained from pentaerythritol halides and base are high (63).

Polymerization of Monomers. The 3,3-disubstituted oxetanes polymerize in the presence of BF_3 (20), PF_5 (33), and some metal alkyl catalysts (157). Farthing (62) found with BF_3 etherate as initiator for the homopolymerization of 3,3-bis(chloromethyl)oxetane, that a trace of water must be present as co-catalyst.

The polymerization of these monomers is usually conducted below room temperature (20) in methyl chloride, sulfur dioxide, or other low-boiling solvents (20, 62), although the polymerization can be

performed at higher temperatures (62). The polymer produced at low temperature is apparently of much higher molecular weight than that produced at elevated temperatures (62).

Polymers of 3,3-bis(chloromethyl)oxetane are inert, highly crystalline compounds from which fibers and films may be drawn (60, 22). The polymers are insoluble in most solvents at room temperature (63, 132) and absorb very little water (158). They have good dimensional stability and may be used as insulating material for electrical conductors and may be molded into gears and valves (20). The polymerization of these monomers was recently reviewed by Eastham (52).

Alkene Sulfides

The alkene sulfides have been used as insecticides (73, 108, 144), and the polymers as components of extreme pressure lubricants (1). The chemistry of alkene sulfides was recently reviewed by Schönberg (159), and was briefly reviewed by Reid (155) and Tarbell and Harnish (168).

Preparation of Monomers. Alkene sulfides may be prepared by treating the corresponding alkylene carbonates or alkene oxides with thiourea or alkali metal thiocyanates (159, 160b). Investigations of Olin and Dains (146) indicate that the reaction with alkene oxides and thiourea may proceed through a 1,3-oxathiolane since with diphenylthiourea an addition product was isolated which could have had the cyclic compound as a precursor (155). Modifications of the thiourea reaction resulting in increased yields have been reported (28, 76).

The mechanism of the reaction of thiocyanate ion with alkene oxides proposed by Ettlinger (60) and van Tamelen (169) was investigated by

Price and Kirk (152).

Alkene sulfides have also been prepared from 1,2-dithiocyanates and sodium sulfide (31), and from ethylene bromide and dimethyl sulfide. A possible mechanism for the latter reaction involving sulfonium ions was proposed by Ray and Levine (154). Alkene sulfides may also be prepared from 2-chloroethyl mercaptans and base (38, 145).

Polymerization of Monomers. Ethylene sulfide polymerizes upon standing (168). The reaction is catalyzed by mineral acids, aqueous ammonia, acetic acid, concentrated aqueous alkali, pyridine, and salts of heavy metals (45, 46). Polyethylene sulfide is a white powder which melts at 140-150°, and is insoluble in ordinary solvents (76). Polymerization is inhibited by mercaptans (39). It is possible that the acid-catalyzed reaction proceeds through an ethylenesulfonium ion, and if so, the mercaptan may react faster with this ion than with ethylene sulfide, which would account for the role of thiols as inhibitors (168). If the polymer contains halogen end groups, it may be depolymerized by heating (14, 139).

Thioepichlorohydrin (75, 77) in the presence of a trace of sulfuric acid polymerizes to a dark-brown solid upon heating. The product is soluble in benzene and has a molecular weight of 1,000. At room temperature the polymer produced is a colorless, transparent resin, soluble only in chloroform.

Propylene sulfide polymerizes to a white, tacky, nonvolatile resin when heated with NaOEt for two hours (134).

Monomer reactivity ratios have been reported for ethylene sulfide and ethylene oxide (47). The ratio for ethylene sulfide is a very large positive number and for ethylene oxide a small negative number. Since the negative ratio obviously has no significance the only conclusion

made was that if the growing copolymer terminates in an ethylene sulfide unit, it has an overwhelming tendency to add another sulfide monomer.

Competitive experiments were performed, and relative reactivities were reported (47). The relative reactivity is the ratio of the rate constants for disappearance of the two monomers. The values reported for ethylene sulfide, propylene sulfide, N-ethylethylenimine, and ethylene oxide were respectively, 215, 215, 5.4, and 1.

KINETICS OF COPOLYMERIZATION

A review (137) and an excellent monograph (3) on copolymerization have been published.

Classical Copolymer Equation

The first studies on the mechanism of copolymerization were made by Dostal (48). Since the development of the classical copolymer equation is presented in most polymer textbooks, the derivation is not included in this dissertation. The equation is:

$$\frac{m_1}{m_2} = \frac{(M_1)}{(M_2)} \frac{r_1 M_1 + M_2}{r_2 M_2 + M_1}$$

where: m_1 and m_2 are the concentrations of monomers M_1 and M_2 in the copolymer at low conversion. (M_1) and (M_2) are the concentrations of the two monomers in the feed. r_1 and r_2 are monomer reactivity ratios.

Reactivity ratios have been determined by three methods: curve fitting (3), Mayo-Lewis (26, 136), and Fineman-Ross method (68). The latter method was used in this investigation. By defining concentrations

in terms of mole fraction, the copolymer composition equation can be rearranged to a linear equation. The slope of the line is r_1 and the intercept, $-r_2$. Several experiments are performed with different concentrations of monomer feed. The reactions are allowed to proceed to low conversion, and the mole fraction of monomer repeating units in the copolymer are determined. Each experiment gives a single point on the plot. The best value of slope and intercept is determined by the method of least squares.

Katchalski-Shalitin Theory

A theory (162) describing the kinetics of copolymerization of NCA's was recently proposed and experimentally verified. The diethylamine-initiated copolymerization of γ-benzyl N-carboxy-L-glutamate anhydride (G) and ε,N-carbobenzoxy-α,N-carboxy-L-lysine anhydride (L) in N,N-dimethylformamide indicated that the rate of copolymerization of G and L was approximately equal to the sum of the rates of homopolymerization of the two monomers when the same amounts of solvent and initiator were used. The rate of copolymerization was slightly greater than the sum of the rates of homopolymerization, probably because of the higher concentration of monomers in the copolymerization reaction mixture (162).

The homopolymerizations of both G and L were found to be first order with respect to the corresponding monomer, and G was approximately 2.5 times as reactive as L. The rate expressions for the homopolymerization of the monomers are:

$$-d[G]/dt = k_G[I]_0[G]$$

and

$$-d[L]/dt = k_L[I]_0[L]$$

where: k_G and k_L = the specific reaction rate constants for G and L respectively.

[G] and [L] = concentration of monomers G and L respectively.

$[I]_0$ = initial concentration of initiator.

-d[G]/dt and

-d[L]/dt = rate of disappearance of G and L.

The corresponding rate expression for copolymerization of G and L was shown to be:

$$-d[G + L]/dt = k_{cop.}[I]_0[G + L]$$

where: $k_{cop.}$ = specific reaction rate constant for copolymerization of G and L.

[G + L] = total concentration of unreacted monomers.

-d[G + L]/dt = rate of disappearance of G + L.

At low conversion, and with the initial concentrations of G and L equal, the expression for $k_{cop.}$ was found to be to a close approximation:

$$k_{cop.} = \frac{k_G + k_L}{2}$$

At high conversion, when most of G had reacted, $k_{cop.}$ was approximately equal to k_L.

When the initial concentrations of G and L were not equal, the rate of copolymerization was still approximately equal to the sum of the rates of homopolymerization, but under these conditions at low conversion the expression for $k_{cop.}$ becomes approximately:

$$k_{cop.} = \frac{k_G[G]_0 + k_L[L]_0}{[G]_0 + [L]_0}$$

It is interesting to note that this expression reduces to the preceding one when $[G]_0 = [L]_0$.

Experiments with several pairs of NCA's were conducted. Of the co-monomers tested only glycine-NCA with G and sarcosine-NCA with G failed to obey the theory. For these monomers, during the latter stage of the reaction the rate of copolymerization was found to be considerably less than the sum of the rates of homopolymerization.

Just as for free radical copolymerization, four propagation reactions and rate expressions may be written for the copolymerization of G and L.

$$L^* + L \xrightarrow{k_{11}} L^*; \text{ rate} = k_{11}[L^*][L]$$

$$L^* + G \xrightarrow{k_{12}} G^*; \text{ rate} = k_{12}[L^*][G]$$

$$G^* + L \xrightarrow{k_{21}} L^*; \text{ rate} = k_{21}[G^*][L]$$

$$G^* + G \xrightarrow{k_{22}} G^*; \text{ rate} = k_{22}[G^*][G]$$

Where: L and G represent unreacted monomers. L* and G* represent growing copolymer molecules with terminal L and G groups respectively. k_{11}, k_{12}, k_{21} and k_{22} are the rate constants for the propagation reactions.

However, since it was shown experimentally that only two rate constants, k_G and k_L, are necessary to describe the copolymerization of G and L, it may be assumed that $k_{11} = k_{21} = k_L$ and $k_{12} = k_{22} = k_G$. Unlike the situation in radical copolymerization (26), the chemical nature of the monomers and not the nature of the reactive end of the growing copolymer molecule determines the rate of copolymerization.

The expressions for the disappearance of L and G during copolymerization are:

$$-d[L]/dt = k_{11}[L^*][L] + k_{21}[G^*][L]$$

$$= k_L[L]([L^*] + [G^*]).$$

and

$$-d[G]/dt = k_{12}[L^*][G] + k_{22}[G^*][G]$$

$$= k_G[G]([L^*] + [G^*]).$$

The ratio of the rates of disappearance of G and L is:

$$\frac{d[G]}{d[L]} = \frac{k_G}{k_L}\frac{[G]}{[L]} = \alpha\frac{[G]}{[L]}$$

where: $\alpha = \frac{k_G}{k_L}$

and $\frac{d[G]}{d[L]}$ = ratio of rates of addition of G and L to the growing copolymer.

Since the ratio of the rates of addition of the two monomers to the growing copolymer is equal to the ratio of the concentration of the two monomers present in the growing copolymer, the expression $d[G]/d[L]$ may be replaced by $\Delta G'/\Delta L'$. This applies only at low conversion, however, since the former expression is a differential and the latter is not.

The preceding equation may be rewritten as:

$$\frac{\Delta G'}{\Delta L'} = \alpha\frac{[G]_0}{[L]_0}$$

where: $\frac{\Delta G'}{\Delta L'}$ = ratio of concentrations of monomers present in the copolymer at low conversion.

$\frac{[G]_0}{[L]_0}$ = ratio of initial concentrations of unreacted monomers.

This equation is the Katchalski-Shalitin copolymer composition equation.

A more useful form of the equation can be derived by defining concentration in terms of mole fraction. If both sides of the equation

are divided by $\Delta G' + \Delta L'$ and $[G]_0 + [L]_0$ the equation becomes:

$$X'_G(X_L) = \alpha (X_G)(X'_L)$$

where: X'_G and X'_L = mole fractions of G and L present in the copolymer at low conversion.

X_L and X_G = mole fractions of G and L in the feed.

By using the relations $X_L = 1 - X_G$ and $X'_L = 1 - X'_G$, and by collecting like terms, the equation becomes (162):

$$X'_G = \frac{\alpha X_G}{1 + (\alpha - 1)X_G}$$

The general equation may be written as:

$$m_1 = \frac{\alpha M_1}{1 + (\alpha - 1)M_1}$$

where: m_1 = mole fraction of M_1 in the growing copolymer at low conversion.

M_1 = mole fraction of M_1 in the monomer feed.

$\alpha = k_{M_1}/k_{M_2}$

If α is known, or can be evaluated experimentally, the composition of the copolymer at low conversion can be calculated from the preceding equation for different values of monomer M_1 in the feed. Katchalski and Shalitin tested this equation for G and L and found excellent agreement between the experimental points and the theoretical curve.

The differential form of this copolymer equation was derived in 1941 by Wall (173) for radical copolymerization. A few α values were reported (133, 135) and seemed to confirm the equation, but further investigations (2, 136, 174) revealed that radical copolymerization was more complex.

EXPERIMENTAL METHODS AND RESULTS

SYNTHESIS AND PROPERTIES OF MONOMERS AND POLYMERS

Preparation and Purification of Monomers

NCA's and OCA's. The NCA's of DL-valine, DL-alanine, γ-benzyl L(+)-glutamate, and anthranilic acid were prepared by the modified Fuchs (74) synthesis. Unsuccessful attempts were made to prepare the NCA's of L(-)-cystine and N-phenylglycine, and the OCA of DL-mandelic acid.

DL-Valine-NCA. A dry, three-neck, 500-ml., round-bottom flask was fitted with a stirrer, a gas inlet tube, and a gas discharge tube. The discharge tube was connected to a series of two gas-washing bottles. The first bottle was empty and the second contained NH_4OH to react with escape gases.

DL-Valine (25 g., 0.21 mole) was added to the flask containing dioxane (250 ml.) which had been refluxed over sodium two days. Stirring was maintained at sufficient rate to keep the amino acid suspended in the dioxane. The temperature of the contents of the flask was increased to 40° and phosgene was bubbled into the suspension. The reaction was complete after two hours as was evidenced by solution of the amino acid. Dry air was passed through the solution for twenty hours to remove HCl and excess phosgene.

The solution was concentrated by distillation under reduced pressure until approximately 75 ml. of straw-colored liquid remained. This liquid was diluted with $CHCl_3$ which had been treated to remove the ethanol stabilizer, and was transferred to a dry 500-ml. Erlenmeyer flask. Approximately 300 ml. of petroleum ether was added to the flask; this caused the immediate precipitation of crude monomer. The flask was stoppered, protected against moisture, and stored in the refrigerator overnight.

Purified-grade ethyl acetate was treated by the procedure of Fieser (67) to remove any moisture present. This procedure involves treatment of the ester with an equal volume of 5 per cent Na_2CO_3, followed by saturated $CaCl_2$ solution, drying over anhydrous K_2CO_3 and distilling, and finally drying over P_2O_5 and distilling.

The crude NCA was isolated by filtration in the hood since residual amounts of phosgene were still present. The NCA was dissolved in the minimum amount of anhydrous ethyl acetate, and petroleum ether was added until the solution became turbid. The flask was stoppered, protected against moisture, and set aside to allow the NCA to precipitate. The flask was then diluted with petroleum ether to a total volume of 450 ml., stoppered, protected against moisture, and stored in the refrigerator overnight.

The white needles were isolated by filtration; yield 21 g. (0.15 mole, 69%), m.p. 76-77° [lit. (98) 81°]. A second recrystallization from ethyl acetate-petroleum ether increased the m.p. to 79-81°.

DL-Alanine-NCA. DL-Alanine (10 g., 0.11 mole) and dry dioxane (200 ml.) were placed in a reaction vessel similar to that described for the preparation of valine-NCA. The reaction was performed as

previously described, but approximately four hours were required for completion of the reaction. After the amino acid had dissolved, additional DL-alanine (10 g., 0.11 mole) was added to the flask. Phosgene was again bubbled into the suspension, and when the reaction was completed the NCA was processed as previously described for valine-NCA. Crude DL-alanine-NCA was first obtained as an oily residue, but solidified when triturated with petroleum ether. The monomer was recrystallized twice from ethyl acetate-petroleum ether and was isolated by filtration. The yield was not determined because of the sensitivity of alanine-NCA to atmospheric moisture; m.p. 44-47° [lit. (98) 45-46°].

γ-Benzyl L(+)-Glutamate-NCA. The procedure of Blout and Karlson (27) was utilized in the preparation of the γ-benzyl ester of L(+)-glutamic acid.

L(+)-Glutamic acid (44 g., 0.30 moles) and 80 ml. of fuming HBr were added to 300 ml. of reagent grade benzyl alcohol. The mixture was stirred with a thermometer and heated on a hot plate for approximately one hour at 60-70° until the amino acid dissolved. This solution was allowed to cool to 35° and was cautiously added to a solution of 80 ml. of pyridine and 590 ml. of ethanol. The product began to precipitate at 28° and the whole reaction mixture was placed in the refrigerator for 22 hours. The precipitate was collected by filtration, washed with ethanol, then with ethyl ether, and allowed to dry. After drying, the crude ester was dissolved in 5 per cent ethanol and the pH was adjusted to 7 by addition of $NaHCO_3$. The solution was filtered and returned to the refrigerator. After 20 hours the ester was recovered by filtration and was washed with distilled H_2O. The precipitate was

washed with ethanol, filtered, washed with ether, filtered, and allowed to dry. The purified product was in the form of white plates; yield 14 g. (0.06 mole, 20%), m.p. 174° [lit. (27) 174°].

γ-Benzyl L(+)-glutamate-NCA was prepared in an apparatus similar to that previously described for valine-NCA. γ-Benzyl L(+)-glutamate (14 g., 0.06 mole) and dry dioxane (250 ml.) were stirred at a rate sufficient to keep the ester in suspension. Phosgene was passed into the suspension for 2.5 hours at which time the ester had completely dissolved. After bubbling dry air through the clear, yellow-tinted solution for 20 hours it was concentrated to 80 ml. by vacuum distillation. The oily residue was diluted with 40 ml. of $CHCl_3$, and n-hexane was added until the solution became turbid. After cooling overnight in the refrigerator only a few crystals of NCA were observed in the flask, so the solution was again concentrated under reduced pressure with the temperature maintained below 45°. The 30 ml. of oily, straw-colored residue was dissolved in a small volume of $CHCl_3$, diluted past turbidity with n-hexane, and stored in the refrigerator overnight. The crystals that appeared were isolated by filtration and were recrystallized from $CHCl_3$-n-hexane and ethyl acetate-n-hexane. After 12 hours in the refrigerator the product was recovered by filtration and was stored in a vacuum desiccator. γ-Benzyl L(+)-glutamate-NCA was obtained as a white crystalline solid; yield 9.5 g. (0.036 mole, 60%), m.p. 92-94° [lit. (27) 93-94°].

Isatoic Anhydride (170). Anthranilic acid (34 g., 0.25 mole) was dissolved with gentle heating in 250 ml. of H_2O and 32 ml. of concentrated HCl. The warm solution was filtered into a 500-ml., 3-neck, round-bottom flask. The flask was fitted with a stirrer, a

gas-dispersion inlet tube, and an outlet tube connected to a second flask charged with NH_4OH.

The solution was rapidly stirred, and phosgene was passed into the flask below the surface of the liquid at a rate sufficient to form several bubbles per second in the NH_4OH scrubber. Isatoic anhydride began to precipitate within 10 minutes. The temperature of the solution was determined and the rate of passage of phosgene was adjusted so that the temperature did not rise above 50°. Phosgene passage was stopped after 15 minutes, dry air was bubbled through the suspension, and crude isatoic anhydride was collected on a Büchner funnel. The solid was washed with three portions of cold H_2O to remove residual phosgene and was set aside to dry.

The mother liquor was returned to the flask, and the apparatus was reassembled after first cleaning the gas-dispersion tip with hot dioxane. Phosgene passage was continued, resulting again in the precipitation of crude isatoic anhydride. The procedure was repeated twice.

The crude isatoic anhydride (17 g.) was dried first at room temperature and then at 100°. It was recrystallized twice from 95 per cent ethanol and was obtained as white crystals; yield 10 g. (0.06 mole, 24%), m.p. (dec.) 242° [lit. (170) 243°].

Attempted Synthesis of L(-)-Cystine-NCA. L(-)-Cystine (20 g., 0.08 mole) and dry dioxane (250 ml.) were added to an apparatus similar to that described for the preparation of valine-NCA. Stirring was maintained at a rate sufficient to keep the amino acid suspended in the dioxane. Phosgene was passed into the suspension for 6 hours without noticeable change in the appearance of the amino acid. Over a period of two additional days phosgene was bubbled into the suspension at intervals while stirring was maintained constantly. After

phosgene had been passed into the suspension for a total time of 10-12 hours, the appearance of the amino acid gradually changed to a pasty, light-tan solid. The flask was set aside in the hood and the suspension allowed to settle. The liquid was decanted and processed as previously reported for valine-NCA, but only a trace of solid material was obtained. The pasty, light-tan solid was treated with $CHCl_3$, found to be insoluble, and was discarded. The NCA has never been prepared by this procedure.

Attempted Synthesis of DL-Mandelic Acid-OCA (43). Mandelic acid (26 g., 0.17 mole) was dissolved in dry dioxane (250 ml.) in an apparatus similar to that described for the preparation of valine-NCA. This acid, unlike the amino acids, is soluble in dioxane. The solution was stirred, and the temperature maintained at 50° for 5 hours during which time phosgene was passed into the flask. Dry air was bubbled into the solution to remove HCl and excess phosgene. The solution was concentrated to 50 ml. by distillation under reduced pressure, and the resulting oil was diluted with 50 ml. of $CHCl_3$. The solution was transferred to a 500-ml. Erlenmeyer flask, and diluted with petroleum ether until it became turbid. The flask was stored in the refrigerator for several days. The solid was isolated by filtration and was recrystallized twice from ethyl acetate-petroleum ether. The white crystalline solid weighing 5.5 g., obtained by filtration, appeared to decompose at 55° without melting and did melt at 121°. A mixed melting point was taken with the product and authentic DL-mandelic acid. The melting point was not depressed indicating that starting material was recovered. It is probable that variations of the procedure would have produced the desired product, but no additional time could be expended on it.

β-Lactones. Reagent grade β-propiolactone and a generous sample

of the β-lactone of 2,2,4-trimethyl-3-hydroxy-3-pentenoic acid, supplied through the courtesy of Dr. R. H. Hasek and Tennessee Eastman Company, were used after vacuum distillation. Attempts to prepare the β-lactone of 2,2,4-trimethyl-3-hydroxy-3-pentanoic acid and β-butyrolactone were unsuccessful.

Attempted Preparation of the β-Lactone of 2,2,4-Trimethyl-3-Hydroxy-3-Pentanoic Acid. Thiophene-free benzene (20 ml.) and the β-lactone of 2,2,4-trimethyl-3-hydroxy-3-pentenoic acid (19 g., 0.14 mole) were added to a clean, dry pressure bottle which had been thoroughly wrapped with tape. PtO_2 catalyst (0.3 g.) was added to the bottle, and it was attached to a Parr hydrogenation apparatus. The system was evacuated by an aspirator and flushed with hydrogen. The system was again evacuated and filled with hydrogen to a gage pressure of 42 lbs./sq. in. The mechanical shaker was started, and within two minutes the hydrogen pressure decreased to 40 lbs./sq. in. Within twenty minutes the pressure decreased to 34 lbs./sq. in., but did not drop further during a two-hour period. The reaction was stopped, and the catalyst was removed by filtration. The solution was fractionally distilled, and the following fractions were collected:

Fraction	Temperature	Weight
1	32-34°/3 mm.	6.78 g.
2	65°/3 mm.	0.37 g.
3	78-82°/3 mm.	3.37 g.

The refractive index of fraction 3 is 1.4329. The reported physical constants (53) for crude 3-hydroxy-2,2,4-trimethyl-3-pentanoic acid β-lactone are: b.p. 75-82°/9 mm., n_D^{20} 1.4220-1.4320. While some of the desired material was probably present, the product was much too impure

to use as monomer.

Attempted Preparation of β-Butyrolactone (164). Freshly distilled diketene (43.8 g., 0.52 mole), ethyl acetate (40 ml.), and 10 per cent Pd on charcoal (0.5 g.) were placed in a round-bottom flask which was connected to a hydrogenation apparatus. The system was evacuated by an aspirator, and was filled with hydrogen. The reduction was performed at 0° and atmospheric pressure. In 12 hours and 45 minutes the theoretical amount of hydrogen was used. The catalyst was removed by filtration, and the solution was distilled at atmospheric pressure to remove the ethyl acetate. The last few ml. of high-boiling liquid decomposed. The crude product was fractionally distilled and the following fractions were collected:

Fraction	Temperature	Weight
1	$28\text{-}30^{\circ}$/4.2 mm.	11 g.
2	$30\text{-}32^{\circ}$/4.2 mm.	15 g.

Determination of the monomer with standard $Na_2S_2O_3$ and I_2 did not give suitable results. The product was not satisfactory for kinetic studies.

Alkene Oxides. Reagent grade propylene oxide was dried over reagent grade KOH pellets and distilled. Reagent grade epichlorohydrin was further purified by distillation.

Aziridines. Generous samples of 1-phenethylaziridine, N-(2-hydroxyethyl)aziridine, and N-(2-hydroxy-n-propyl)aziridine were supplied by the Texas Division of the Dow Chemical Company. These samples and commercial N-ethylaziridine were purified by vacuum distillation. However, N-phenethylaziridine was not polymerized rapidly enough by acid catalysts at room temperature to give useful kinetic

results, and the one N-ethylaziridine-propiolactone copolymer made was an oil and therefore not further studied.

3,3-bis(Halomethyl)oxetanes. A generous sample of 3,3-bis(chloromethyl)oxetane (BCMO) was supplied through the courtesy of Dr. Harold Spurlin and the Hercules Powder Company. BCMO was purified by vacuum distillation. 3,3-bis(Iodomethyl)oxetane (BIMO) was synthesized, but attempts to prepare 3,3-bis(fluoromethyl)oxetane (BFMO) were not successful.

BIMO (34). Freshly distilled BCMO (20 g., 0.13 mole), NaI (47 g., 0.31 mole), and reagent grade 2-butanone (200 ml.) were added to a 3-neck, 500-ml., round-bottom flask fitted with a reflux condenser and stirrer. The suspension was rapidly stirred and was refluxed for 6 hours. Stirring was continued overnight. The suspension was allowed to reflux for an additional 12 hours. The flask was allowed to cool, and the NaCl was removed by filtration. The filtrate was evaporated and the crude BIMO was collected and recrystallized from cyclohexane. The product was obtained as dense, slightly yellow crystals; yield 27 g. (0.08 mole, 62%), m.p. 48.2-49.2° [lit. (34) 50°]. A second recrystallization from cyclohexane yielded colorless crystals melting at 50-51°.

BFMO (59). Potassium fluoride was dried by heating in a furnace at 450° for 5 hours. The salt was allowed to cool by storing in a desiccator overnight. Ethylene glycol (200 ml.), BCMO (55 g., 0.35 mole), and dry KF (50 g., 0.86 mole) were placed in a 500-ml., 3-neck, round-bottom flask. The flask was fitted with a stirrer, a Dean-Stark trap with reflux condenser, and a thermometer which was immersed in the suspension. The suspension was vigorously stirred, and was refluxed gently for 6 hours. The temperature was increased slightly to allow

product to slowly distill into the trap. Two layers should form (59), the lower one being BFMO. Slow distillation was continued for several hours until approximately 100 ml. was collected. The material collected in the trap was completely homogeneous. The reaction was stopped, and the product was not further processed.

In an apparatus similar to that described in the preceding paragraph were placed anhydrous NaF (45 g., 1.07 mole), BCMO (60 g., 0.39 mole), and ethylene glycol (160 ml.). The suspension was stirred rapidly and refluxed gently so that product and ethylene glycol slowly distilled. The product began to distill at a distillation-pot temperature of 150° which was increased to 180° during 7 hours 30 minutes. Crude product (20 g.) was collected as a lower layer in the Dean-Stark trap. The product was washed with twice its volume of distilled H_2O. The organic layer was separated, dried over anhydrous $MgSO_4$ overnight, and distilled at reduced pressure. The product was obtained as a colorless liquid; b.p. 137-138°/76 mm. [lit. (59) 56°/29 mm.]. The boiling point indicated that starting material had probably been recovered. A sample of the product was subjected to sodium fusion and then tested for chloride ion with $AgNO_3$. Results were positive, indicating that starting material had been recovered.

Alkene Sulfides. Only propylene sulfide was used in this investigation.

Propylene Sulfide (47). Potassium thiocyanate (97 g., 1.0 mole) and an equal weight of distilled H_2O were added to a 1-liter Morton flask immersed in an ice-salt bath. The flask was fitted with a stirrer, reflux condenser, and an addition funnel containing propylene oxide (29 g., 0.5 mole). The propylene oxide was added to the flask over a

30-minute period as vigorous stirring was maintained. After 12 hours stirring at 0° the reaction was stopped. The contents of the flask were transferred to a separatory funnel. Two layers formed in the funnel; the lower layer was discarded and the upper layer transferred to a dry Erlenmeyer flask. After drying overnight over anhydrous Al_2O_3, the solution was filtered and rapidly distilled. The crude propylene sulfide (25 g.) was fractionally distilled, and several milliliters of low-boiling product were discarded. The product collected was a colorless liquid; yield 15 g. (0.20 mole, 40%), b.p. 73°/740 mm. [lit. (47) 73-73.6°/738 mm.].

Synthesis and Properties of Homopolymers and Copolymers

Poly-DL-valine. DL-Valine-NCA (6 g., 0.04 mole) was dissolved in dioxane in an Erlenmeyer flask. Methanolic sodium hydroxide initiator (1.10 ml., 0.1502 N) was added, and the solution was protected against moisture with a $CaCl_2$ drying-tube. Within two hours the solution assumed a milky-gel appearance as polypeptide began to precipitate. After 22 days at room temperature the solid was isolated by filtration and was washed with ether; yield 4.2 g. (100%), $\lambda_{max.}$ 3.1, 6.1, 6.55 μ (KBr pellet).

The polymer was dried in a vacuum oven at 120° for 4 hours and was analyzed for nitrogen by a modified ASTM procedure (5,140). The results obtained with three samples were 13.0, 13.6, and 13.6 per cent. The literature (98) reports 13.3 per cent, and the theoretical value is 14.1 per cent.

Experiments designed to find a more suitable solvent for the

homopolymerization of valine-NCA were performed. Valine-NCA (3 g., 0.02 mole) was added to each of three flasks containing respectively, anisole (110 ml.), $CHCl_3$ (60 ml.), and ethyl acetate (60 ml.). A few drops of methanolic sodium hydroxide were added to each flask. After 6 hours the contents of the flask containing anisole were very slightly turbid. At this time the material in the flask containing $CHCl_3$ had gelled, and a definite precipitate had formed in the flask containing ethyl acetate. Five days later the appearance of the material in the flask containing anisole confirmed that solvent to be more satisfactory for homogeneous polymerization of valine-NCA than $CHCl_3$, ethyl acetate, or dioxane.

Valine-NCA (5.00 g., 0.035 mole) was dissolved in anisole in a 250-ml. Erlenmeyer flask. A few drops of triethylamine catalyst were added to the flask. The flask was protected against moisture and placed in a constant-temperature bath at 35°. Polymerization was allowed to proceed for 20 hours, and the polymer was precipitated by slowly pouring the solution into rapidly stirred ether. The polypeptide was isolated by filtration; yield 3 g. (87%). The polymer was washed with 50 per cent methanol (300 ml.), methanol (300 ml.), and ether (300 ml.). After drying at room temperature, the white solid was dried in a vacuum oven at 120° for 3 hours. Nitrogen analysis was performed by the micro-Kjeldahl procedure by the author, also by the micro-Dumas method by Midwest Microlabs, Inc., and by the Texas Division of the Dow Chemical Company. Anal. Calcd. for C_5H_9NO: C, 60.6; H, 9.1; N, 14.1.

Found: N, 13.0 (author)

C, 60.2, 59.9; H, 9.6, 9.4; N, 13.7

(Midwest Microlab)

N, 13.3 (Dow)

N, 13.3, lit. (98)

Polypropiolactone. β-Propiolactone (6.08 g., 0.08 mole) was added to dioxane (200 ml.) in an Erlenmeyer flask. Methanolic sodium hydroxide was added to the flask. The total monomer-to-initiator mole ratio was 100. The reaction was conducted at room temperature. After 22 days the crude polyester (3.7 g., 61%) was isolated by filtration. The polymer was dissolved in hot acetone and precipitated by dilution with H_2O; yield 2.9 g. (48%), $\lambda_{max.}$ 5.78, 8.5μ (KBr pellet). The properties of this polymer are similar to those reported in the literature for polypropiolactone (90).

Copolymers of DL-Valine-NCA and β-Propiolactone. DL-Valine-NCA (17 g., 0.12 mole), β-propiolactone (42.8 g., 0.60 mole), and a mixture of benzene (100 ml.) and anisole (150 ml.) were placed in a 500-ml., round-bottom flask fitted with a reflux condenser. Pyridine catalyst (0.28 g., 3.5 millimoles) was added, and the solution was heated at approximately 70° for 68 hours. The solution was slowly added with vigorous stirring to 3 l. of petroleum ether. The tacky material was recovered from the petroleum ether and partially dissolved in acetone. The solution was slowly added to rapidly stirred ether (500 ml.). The copolymer precipitated as a fine white powder, and was isolated on a medium-frit glass filter; yield 16.2 g. (27%), softening point 70°, $\lambda_{max.}$ 3.0, 5.75, 6.1, 6.5 μ (KBr pellet). The bands indicate ester and amide functional groups.

The copolymer was analyzed for nitrogen by the micro-Kjeldahl procedure. The results obtained were 2.22, 2.11, and 2.05 per cent. The average nitrogen content in the copolymer was 2.13 per cent.

The compound was shown to be a copolymer rather than a mixture of homopolymers by extraction with boiling acetone. A one-gram sample was extracted 6 times with 30-ml. portions of boiling acetone. Two extractions dissolved most of the copolymer. Infrared spectra were obtained of the insoluble residue after 2, 4, and 6 extractions. The spectrum, after 6 extractions, indicated the presence of ester (5.75 μ) and peptide (3.08, 6.12, 6.52 μ). The ratios of intensity of amide (6.12 μ) to ester (5.75 μ) bands after 2 and 6 extractions respectively were 2.7 and 2.6. This technique of establishing the copolymeric nature of a product has been used before (123a, 137a).

A mixture of polyvaline (0.1678 g.) and polypropiolactone (0.8564 g.) was prepared and thoroughly mixed. Since this polyvaline had been found to contain 13 per cent N, the resulting mixture contained 2.13 per cent N. Treatment of the mixture in a manner similar to that previously described for the copolymer indicated that 2 extractions removed the polyester from the mixture. After 2 and 4 extractions of the mixture the infrared spectrum showed only a slight shoulder at 5.75 μ which is also present in the spectrum of polyvaline. Figure 1 is a reproduction of the infrared spectra between 5 and 7 μ of polyvaline, polypropiolactone, copolymer after 6 extractions, and mixture of homopolymers after 4 extractions. These spectra show that polyester can be completely extracted from the mixture.

Solutions of the copolymer in volumetric flasks in a constant-temperature bath at 35° were prepared by diluting to volume with

N,N-dimethylformamide also at 35°. The average efflux times of the solutions through an Ostwald viscometer were determined. The data are summarized in Table I and plotted in Figure 2.

TABLE I

VISCOSITY DATA FOR A COPOLYMER PREPARED FROM β-PROPIOLACTONE AND DL-VALINE-NCA (MOLE RATIO OF MONOMERS, 5 TO 1)

Concentration, g./100 ml.	Efflux time, seconds	$\eta_{sp.}$	$\eta_{sp.}/C$
0.9876	127.8	0.063	0.064
0.6502	125.7	0.046	0.071
0.4938	123.5	0.027	0.055
0.2469	122.0	0.015	0.061
solvent	120.2	---	---

The intrinsic viscosity, ($[\eta]$), determined by extrapolation of the specific viscosity (η_{sp}) divided by concentration (C) to infinite dilution, is 0.05. The copolymer is obviously of low molecular weight.

The number-average molecular weight of the copolymer was determined by dissolving the sample in $CHCl_3$-anhydrous methanol and titrating with standard methanolic potassium hydroxide (0.0938 N) to the phenolphthalein end-point. Titration was performed with a microburette. The end-point was sharp and reproducible, but faded within 20 seconds. The results obtained were 1177, 1106, and 1177.

Another copolymer was prepared from the two monomers using a large excess of β-propiolactone. β-Propiolactone (35.2 g., 0.5 mole), valine-NCA (1.00 g., 0.01 mole), anisole (170 ml.), and methanolic sodium hydroxide (2.9 ml., 0.6169 N) were added to an Erlenmeyer flask,

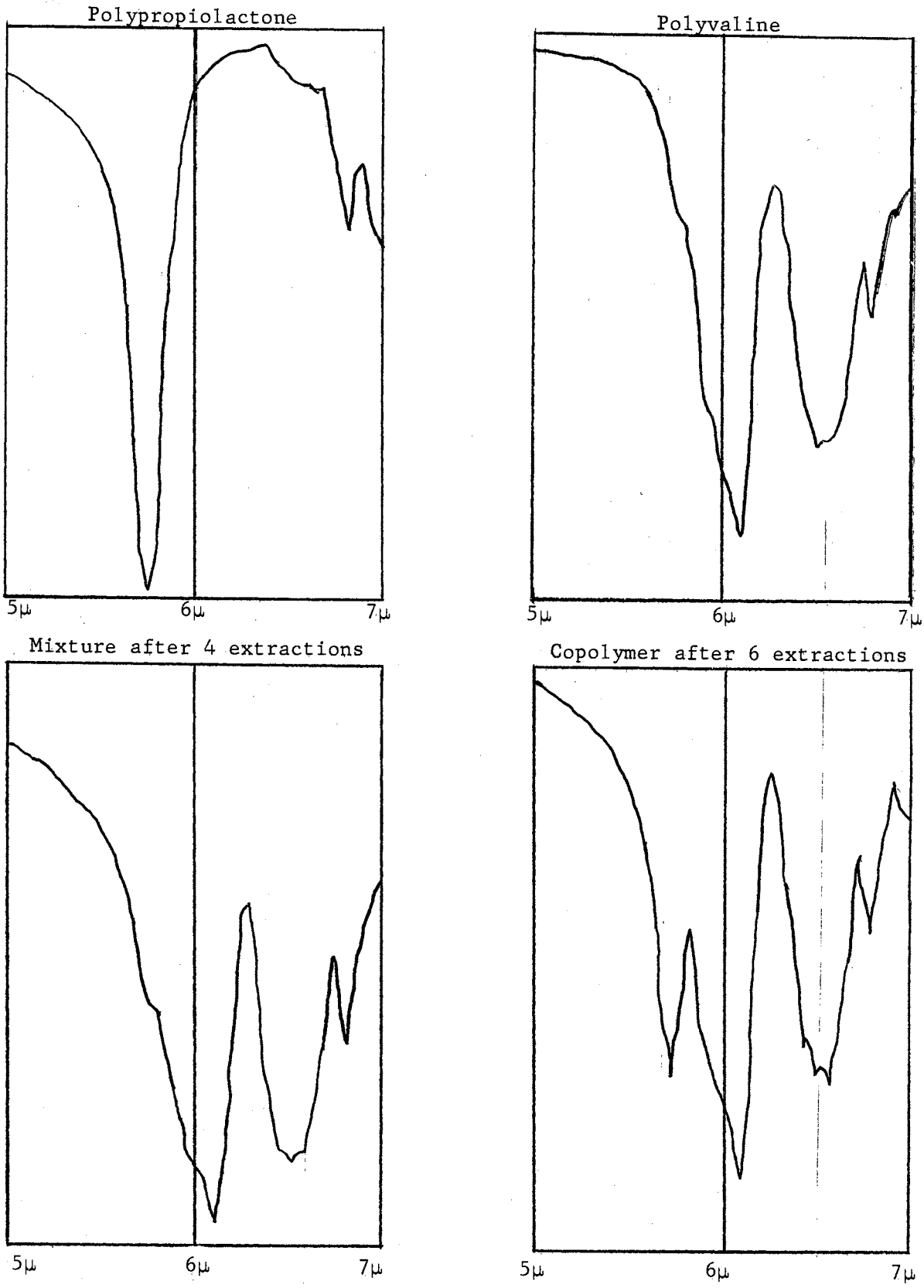


Figure 1. Infrared Spectra (5-7μ) for Polymers of DL-Valine-NCA and β-Propiolactone.

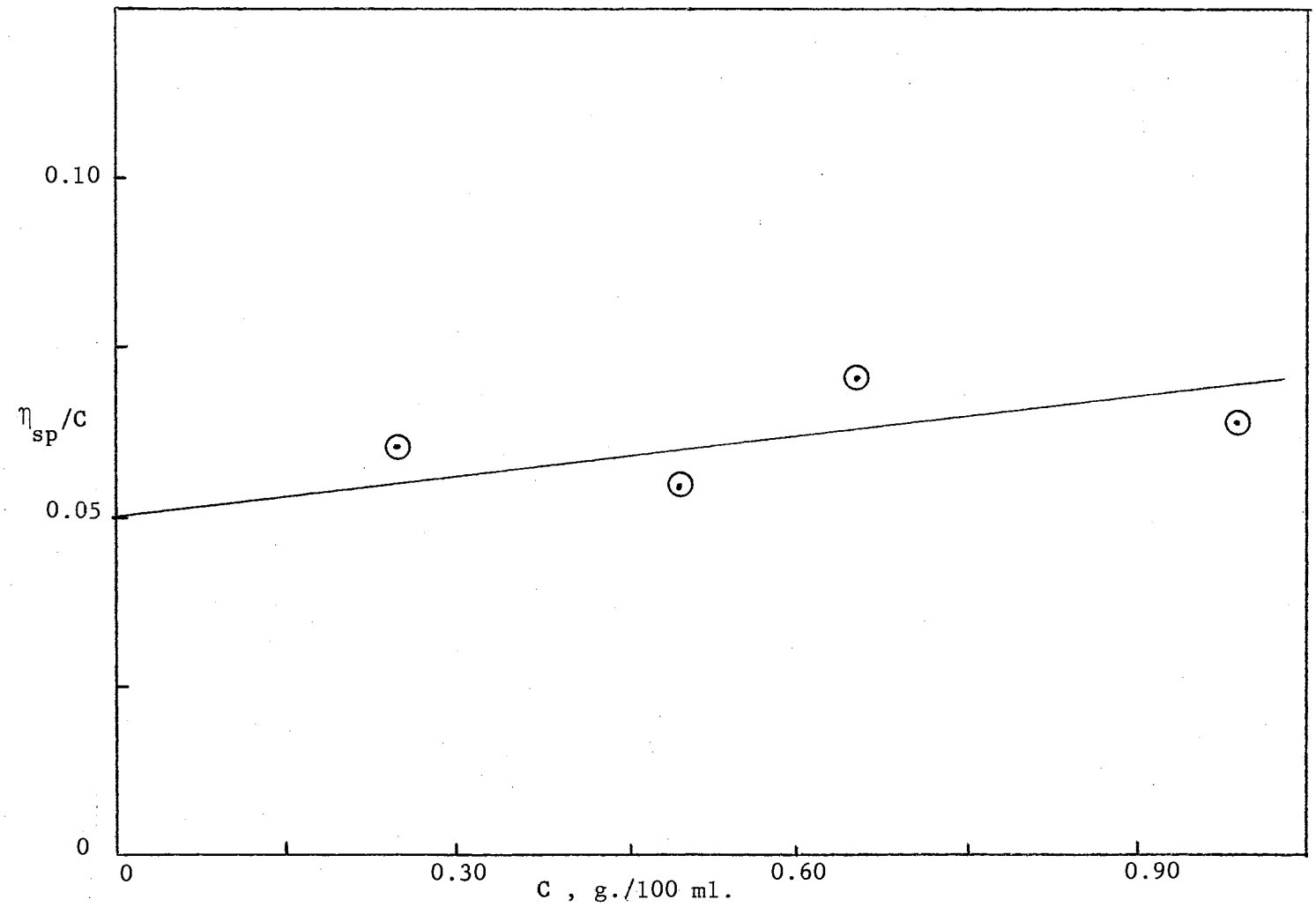


Figure 2. Reduced Viscosity-Concentration Curve for a Copolymer of β-Propiolactone and DL-Valine-NCA (Mole Ratio of Monomers, 5 to 1).

and the solution was stirred with a magnetic stirrer. After seven days at room temperature the copolymer was precipitated by slowly pouring the solution into rapidly stirred ether. The white powder was isolated by filtration on a medium-frit glass filter. The solid was washed by stirring with 3 portions (300 ml.) of ether, filtered and allowed to dry; yield 20.5 g. (57%), softening point 85°.

The number-average molecular weight of the copolymer was determined by titration with methanolic potassium hydroxide as before. The average of three samples was 3,550. Although this value is larger than for the previously reported copolymer, it is still not great enough to suggest useful properties.

Solutions of the copolymer in volumetric flasks in a constant-temperature bath at 35° were prepared by diluting to volume with m-cresol also at 35°. The average efflux times of the solutions through a modified Ubbelohde viscometer were determined at 35°. The data are summarized in Table II and plotted in Figure 3.

TABLE II

VISCOSITY DATA FOR A COPOLYMER PREPARED FROM β-PROPIOLACTONE AND DL-VALINE-NCA (MOLE RATIO OF MONOMERS, 50 TO 1)

Concentration, g./100 ml.	Efflux time, seconds	η_{sp}	η_{sp}/C
1.0126	184.0	0.157	0.155
0.6076	173.6	0.092	0.151
0.3038	166.3	0.046	0.151
0.1519	162.5	0.022	0.145
solvent	159.0	---	---

The value of the intrinsic viscosity determined from Figure 3 is 0.145. Although this value is small, it is greater than that for the preceding copolymer.

Copolymers of DL-Alanine-NCA and β-Propiolactone. DL-Alanine-NCA (2 g., 0.02 mole), β-propiolactone (4.5 g., 0.06 mole), and diethylamine (0.5 ml.) were dissolved in anisole (250 ml.) in a 500-ml. Erlenmeyer flask. The solution was stirred with a magnetic stirrer at room temperature for 119 hours. The copolymer was precipitated by slowly pouring the solution into rapidly stirred ether. The product was isolated by filtration and dried; yield 1 g. (18%), $\lambda_{max.}$ 5.75, 6.1, 6.6 μ (KBr pellet), Found: N, 12.3, 12.2, 12.2. The infrared spectrum indicates the presence of both ester and amide groups.

A block copolymer was prepared by addition of polyalanine (1 g.) to anisole (200 ml.), stirring the suspension for 1 hour to allow the polymer to "swell", and adding β-propiolactone (11.4 g.). The polymerization was allowed to proceed for 6 days, and the polymer was precipitated by slowly adding the suspension to rapidly stirred ether. Efforts to purify the tan solid were unsuccessful, and resulted in considerable loss of product; yield 2 g. (16%), softening point 75°, $\lambda_{max.}$ 3.02, 5.75, 6.1, 6.6 μ (KBr pellet). Found: N, 3.7, 3.7. Infrared spectrum and N analysis indicate that the product is a copolymer.

Attempted Polymerization of Isatoic Anhydride. Isatoic anhydride (3 g., 0.02 mole) was dissolved in dioxane (200 ml.). Methanolic potassium hydroxide (0.1 ml., 0.62 N) catalyst was added, and the solution was stirred for 5 days at room temperature. The solution was slowly added to rapidly stirred ether, but no precipitate formed. This solution was evaporated and the solid recovered and recrystallized

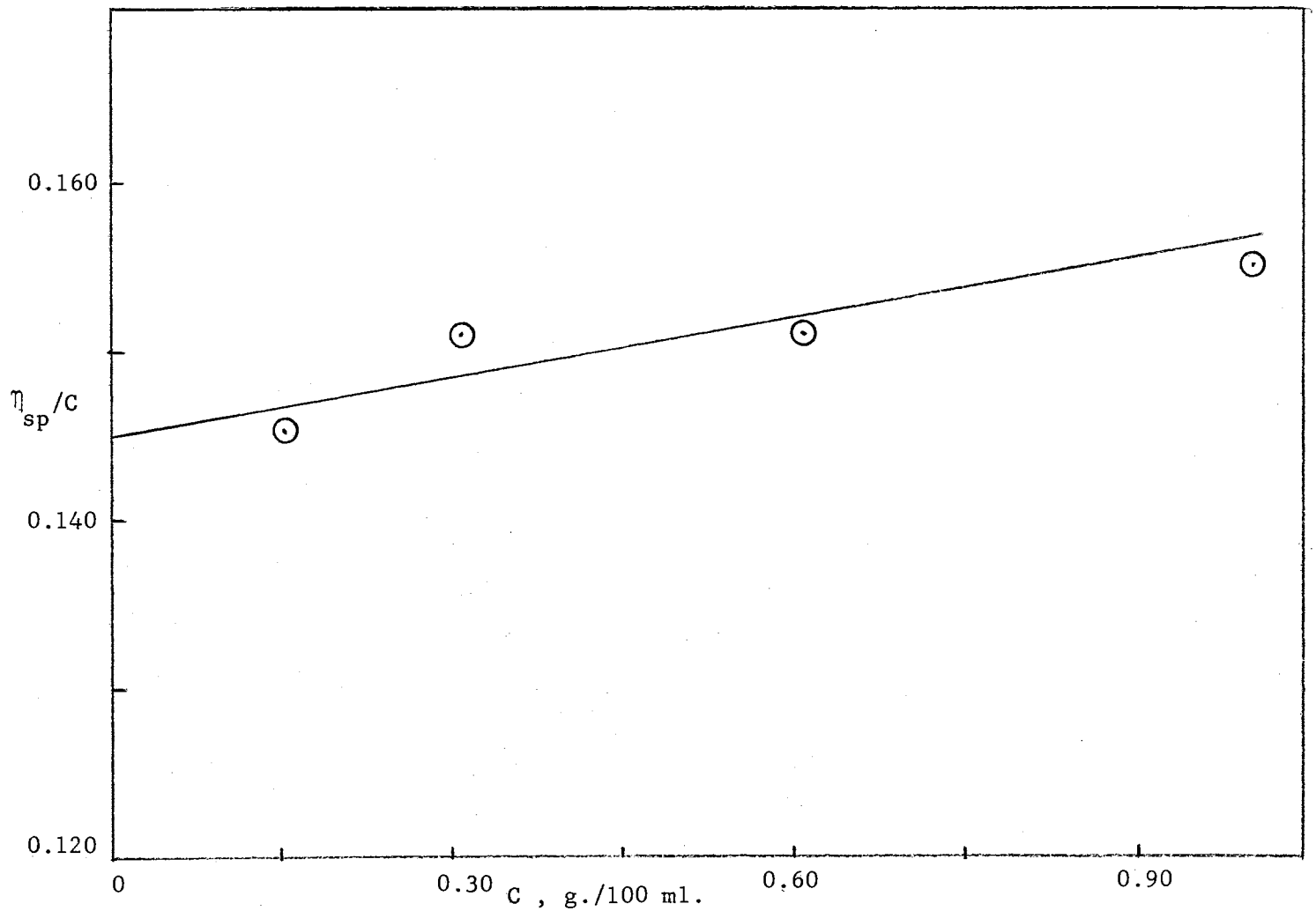


Figure 3. Reduced Viscosity-Concentration Curve for a Copolymer of β-Propiolactone and DL-Valine-NCA (Mole Ratio of Monomers, 50 to 1).

from hot ethanol. The solid was isolated by filtration and dried. It melted at 241° and did not depress the melting point when mixed with authentic isatoic anhydride.

The reaction was repeated using isatoic anhydride (1 g., 0.01 mole) and a few drops of KOH initiator in dioxane (100 ml.). The solution was refluxed for 3 days, and slowly added to rapidly stirred ether. Precipitation did not occur.

Attempted Copolymerization of β-Propiolactone and Propylene Sulfide. Propylene sulfide (7.3 g., 0.1 mole) and β-propiolactone (10.9 g., 0.15 mole) were placed in a 500-ml. Erlenmeyer flask. The two monomers were miscible, and no exothermic reaction occurred upon mixing. Freshly distilled N,N-dimethylformamide (180 ml.) and triethylamine (0.30 ml.) were added to the flask, and the solution was stirred with a magnetic stirrer. After 17 hours a small portion of the product was precipitated by slow addition to excess ether. A white solid immediately formed. It was isolated by filtration, washed with ether, and air-dried; softening point 74°, $\lambda_{max.}$ 5.76 μ. The infrared spectrum was very similar to that of polypropiolactone. The reported softening point of the polyester is 86° (90).

The remainder of the product was precipitated by pouring into rapidly stirred ether after two days total reaction time. The white solid was isolated by filtration, washed with ether (300 ml.), filtered, and dried; yield 6.4 g. (35%). The solid was fused with sodium and the product tested for sulfide ion. The results were negative. Softening point and infrared spectrum proves that the solid product is a homopolymer of β-propiolactone. The test for sulfide ion proves a copolymer was not prepared and also that propylene sulfide did not

homopolymerize to solid polymer.

KINETICS

Classical Copolymer Equation

Determination of Monomer Reactivity Ratios for DL-Valine-NCA and β-Propiolactone. DL-Valine-NCA used in the determination of monomer reactivity ratios was recrystallized twice from ethyl acetate-petroleum ether, and was dried in a vacuum oven at room temperature for at least four hours. Drying at higher temperatures resulted in some decomposition of the monomer. After a few trials it was apparent that even at room temperature slight decomposition gradually occurred. Typically, of 6 g. of monomer, 0.1 g. was found to be insoluble in anisole. Therefore the weight of valine-NCA in solution was determined from the difference of the original weight and the weight of the insoluble residue.

The general procedure used in the investigation was to weigh carefully the required amount of valine-NCA. This monomer was then dissolved in freshly distilled anisole (200 ml.) in a clean, dry 500-ml. Erlenmeyer flask. The insoluble residue was removed by filtration on a medium-frit glass filter, dried, and weighed. The clear solution was returned to the flask, and the calculated weight of freshly distilled β-propiolactone (d^{25} 1.1420 g./ml.) added from a pipette. The flask was placed in a constant-temperature bath at 35.0°. After thermal equilibrium was established, the calculated weight of triethylamine (d^{25}

0.7229 g./ml.) was added from a 1.00-ml. Mohr pipette. In each run the total monomer-to-initiator ratio was approximately 200. Polymerization was allowed to proceed to low conversion. This was accomplished by frequently withdrawing aliquots (1.00 ml.), adding these to rapidly stirred ether (25 ml.), and observing whether precipitation occurred. When the test indicated that polymerization had begun, the reaction was stopped by slowly pouring the anisole solution into rapidly stirred ether (500 ml.). The copolymer was isolated by filtration on a medium-frit glass filter, dried, and weighed. The product was purified by stirring with 3 portions of ether (150 ml.). The fine, white powder was isolated by filtration, dried at room temperature, and stored in a desiccator. The data obtained are presented in Table III.

The copolymers were dried in a vacuum oven for several hours at 70-120°, and analyzed for nitrogen by the micro-Kjeldahl procedure. From the percentage of nitrogen in the copolymer, the mole fraction of valine-NCA repeating unit in the copolymer at low conversion was calculated, assuming 13.6 per cent N, the observed value in the repeating unit of polyvaline, rather than the theoretical value of 14.1 per cent N. These data are presented in Table IV.

Monomer reactivity ratios were determined by the Fineman-Ross method. The form of the equation (69) used in the calculations of r_1 and r_2 is:

$$\frac{f_1(1 - 2F_1)}{(1 - f_1)F_1} = r_2 + \frac{f_1^2(F_1 - 1)}{(1 - f_1)^2F_1} r_1$$

where: f_1 = mole fraction of valine-NCA in the monomer feed.

TABLE III

DATA FOR THE COPOLYMERIZATION OF DL-VALINE-NCA AND β-PROPIOLACTONE TO LOW CONVERSION

DL-Valine-NCA, millimoles	20.90	20.90	41.58	42.12	42.13	41.29
β-Propiolactone, millimoles	377.18	148.97	166.40	77.81	23.72	10.30
Mole fraction of DL-valine-NCA in monomer feed	0.053	0.123	0.200	0.351	0.639	0.800
Volume of triethylamine, ml.	0.28	0.11	0.11	0.08	0.04	0.03
Time of polymerization, hrs.	44	22	19	---	1.75	1.50
Weight of copolymer, g.	0.5551	1.2555	1.7963	0.6755	0.5318	0.5035
Conversion, per cent	1.9	9.8	11.2	6.9	9.0	10.4

TABLE IV

CALCULATION OF MOLE FRACTION OF DL-VALINE-NCA REPEATING UNIT IN THE COPOLYMER OF DL-VALINE-NCA AND β-PROPIOLACTONE

Mole fraction of DL-valine NCA in monomer feed	Nitrogen per cent	Nitrogen per cent average	Mole fraction of valine repeating unit in copolymer
0.053	9.19 9.20 9.29 9.30	9.25	0.607
0.123	11.79[a] 12.05 12.01 12.04	12.03	0.848
0.200	12.56 12.53 12.57 12.39[a]	12.55	0.896
0.351	12.72[a] 12.92 12.88 12.90	12.90	0.931
0.639	13.07 13.11 13.00 12.97	13.04	0.944
0.800	13.57 13.41 13.26 13.39	13.41	0.981

[a]These values were not included in the average.

F_1 = mole fraction of valine-NCA repeating unit in the copolymer at low conversion.

r_1 = monomer reactivity ratio for valine-NCA

r_2 = monomer reactivity ratio for β-propiolactone.

The calculations are presented in tabular form in the Appendix I. For the six experiments performed, the following six linear equations were obtained.

$$0.0197 = 0.0020r_1 - r_2$$

$$0.1151 = 0.0035r_1 - r_2$$

$$0.2210 = 0.0073r_1 - r_2$$

$$0.5007 = 0.0217r_1 - r_2$$

$$1.6649 = 0.1866r_1 - r_2$$

$$3.9225 = 0.3112r_1 - r_2$$

The method of least squares (167) was applied to these equations to determine the best values of r_1 and r_2. These calculations are presented in Appendix II. The values obtained for the slope and intercept are 11 and 0.16 respectively. The corresponding values of the monomer reactivity ratios are: $r_1 = 11$; $r_2 = -0.16$. The least squares straight line and the experimental points are presented in Figure 4.

Katchalski-Shalitin Theory

Experiments were performed with various monomers to determine if the rate of copolymerization was equal to the sum of the rates of homopolymerization.

Base-Catalyzed Polymerization

A number of strong bases were prepared as possible catalysts for homogeneous polymerizations in non-hydroxylic organic solvents. Alkali metal alkoxides were prepared by dissolving the alkali metal in the appropriate alcohol and evaporating the excess solvent. The bases prepared include: $LiOC_2H_4OC_2H_5$, $KOC(CH_3)_3$, $LiOC(CH_3)_3$, $LiOCH_3$, and $NaOCH_3$.

Cetyldimethylethylammonium isopropoxide was prepared by reacting cetyldimethylethylammonium bromide with $NaOCH(CH_3)_2$ in anhydrous isopropyl alcohol, evaporating most of the solvent at room temperature, removing NaBr by filtration, and evaporating the remainder of the alcohol. Last traces of solvent were removed by drying the product over pellet KOH in a desiccator.

A solution of n-butyllithium (83) in ether was also prepared. A dry, 500-ml., three-neck, round-bottom flask was fitted with a stirrer, an addition funnel, and a reflux condenser. The flask was placed in an ice-salt bath and was flushed with nitrogen. Anhydrous ether (150 ml.) and finely cut Li (2.1 g., 0.33 mole) were added to the flask. A solution of n-butyl bromide (17 g., 0.12 mole) in anhydrous ether was added from the addition funnel over a 45-minute period. Nitrogen was passed over the surface of the solution throughout the reaction. Shortly after the first portion of n-butyl bromide was added, LiBr began to precipitate. Stirring was continued for seven hours and the solution was filtered through glass wool. The unreacted Li (0.3 g., 0.05 mole) was isolated, but most of the LiBr went through the glass wool. The solution was transferred to a clean, dry flask, flushed with

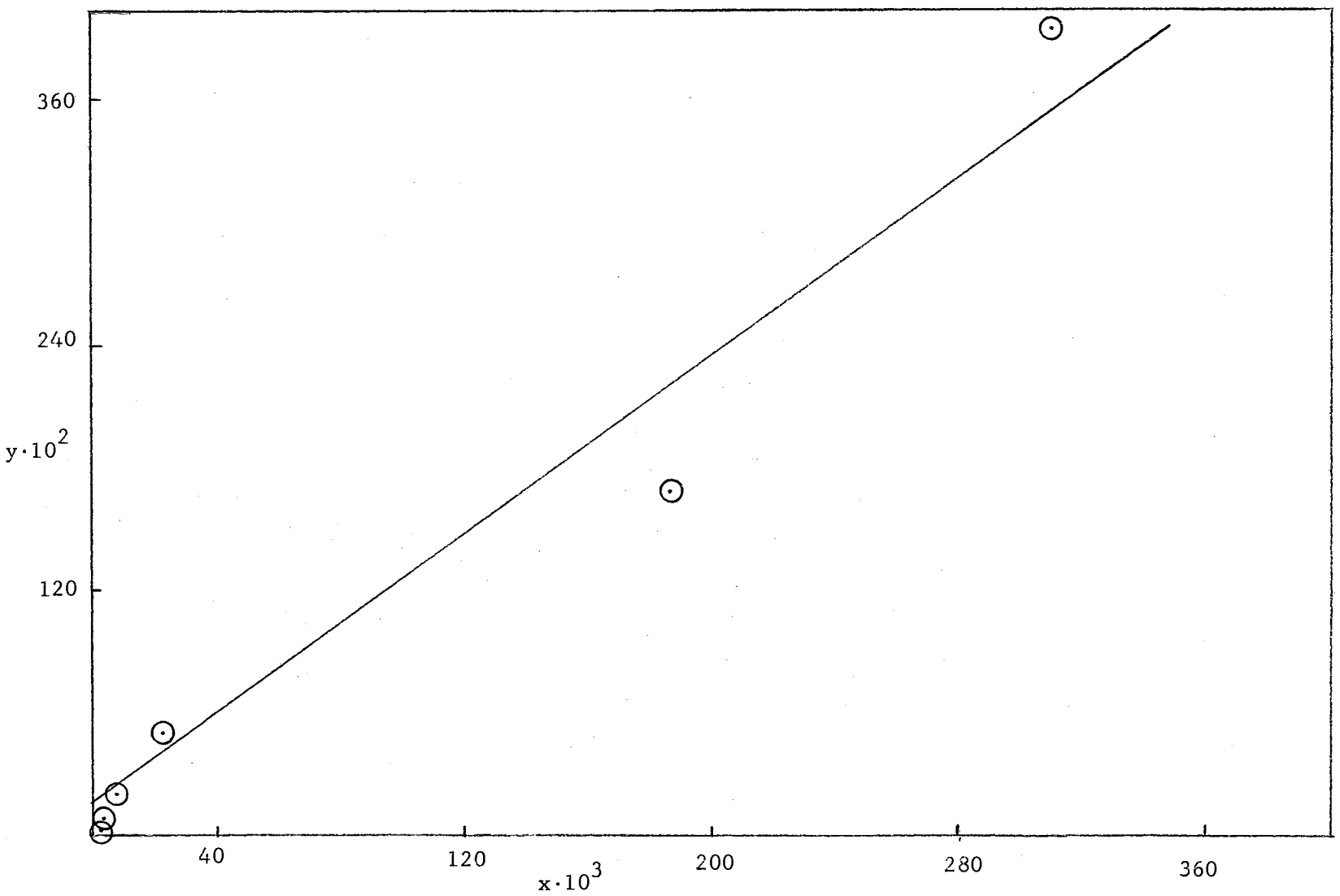


Figure 4. Fineman-Ross Plot for DL-Valine-NCA and β-Propiolactone.

nitrogen, protected against moisture, and stored in the refrigerator overnight. The solution was decanted and the solid discarded. The last traces of LiBr were removed by filtration through a dry, medium-frit glass filter. The solution was transferred to a clean, dry reagent bottle, flushed with nitrogen, protected against moisture, and stored in the refrigerator.

Homopolymerization of β-Propiolactone. β-Propiolactone (10 ml., 11.42 g.) was transferred to a 200-ml. volumetric flask by means of a 10.00-ml. pipette. The lactone was diluted with reagent grade acetonitrile and the flask was placed in a constant-temperature bath at 55°. After thermal equilibrium was established, the flask was diluted to volume with acetonitrile also at 55°. The contents of this flask and an additional 200 ml. of acetonitrile were transferred to a 500-ml., three-neck, round-bottom flask fitted with a stirrer and a reflux condenser.

After thermal equilibrium was established at 55° a 5.00-ml. aliquot of the solution was withdrawn and transferred to a 250-ml. Erlenmeyer flask containing excess standard $Na_2S_2O_3$ solution. Diethylamine initiator (0.10 ml., 0.0709 g.) was added to the round-bottom flask as the stop watch was started. Aliquots (5.00 ml.) were taken at known times and transferred to 250-ml. Erlenmeyer flasks containing excess standard $Na_2S_2O_3$ solution (0.0982 N). These solutions were stirred with a magnetic stirrer for 30 minutes, and were back-titrated with standard iodine solution (0.1072 N). The results obtained are presented in Table V.

These data are plotted as a pseudo first-order reaction in Figure 5. The slope of the line of Figure 5 is -3.0×10^{-4}. The rate

constant for the pseudo first-order reaction is: $k_{55^o} = 6.9 \times 10^{-4} min.^{-1}$

TABLE V

RATE OF BASE-CATALYZED HOMOPOLYMERIZATION OF β-PROPIOLACTONE AT 55° IN ACETONITRILE

Time, minutes	Concentration of unreacted β-propiolactone, eq./l.
0	0.3515
30	0.3272
210	0.2795
360	0.2497
1034	0.1614
1339	0.1379
1639	0.1108
1796	0.1026

In this investigation, several solvents were tried as homogeneous polymerization media for valine-NCA and β-propiolactone. β-Propiolactone was found to homopolymerize too slowly in anisole for kinetic studies to be undertaken. However, dimethyl sulfoxide was found to be a suitable solvent for the homopolymerization of β-propiolactone.

β-Propiolactone (2.00 ml., 2.28 g.) was transferred to a 200-ml. volumetric flask containing dimethyl sulfoxide. The volumetric flask was placed in a constant-temperature bath at 55°. After thermal equilibrium was established, the flask was diluted to volume with dimethyl sulfoxide at 55°. The contents of the volumetric flask were transferred to a 500-ml., 3-neck, round-bottom flask, fitted with a reflux

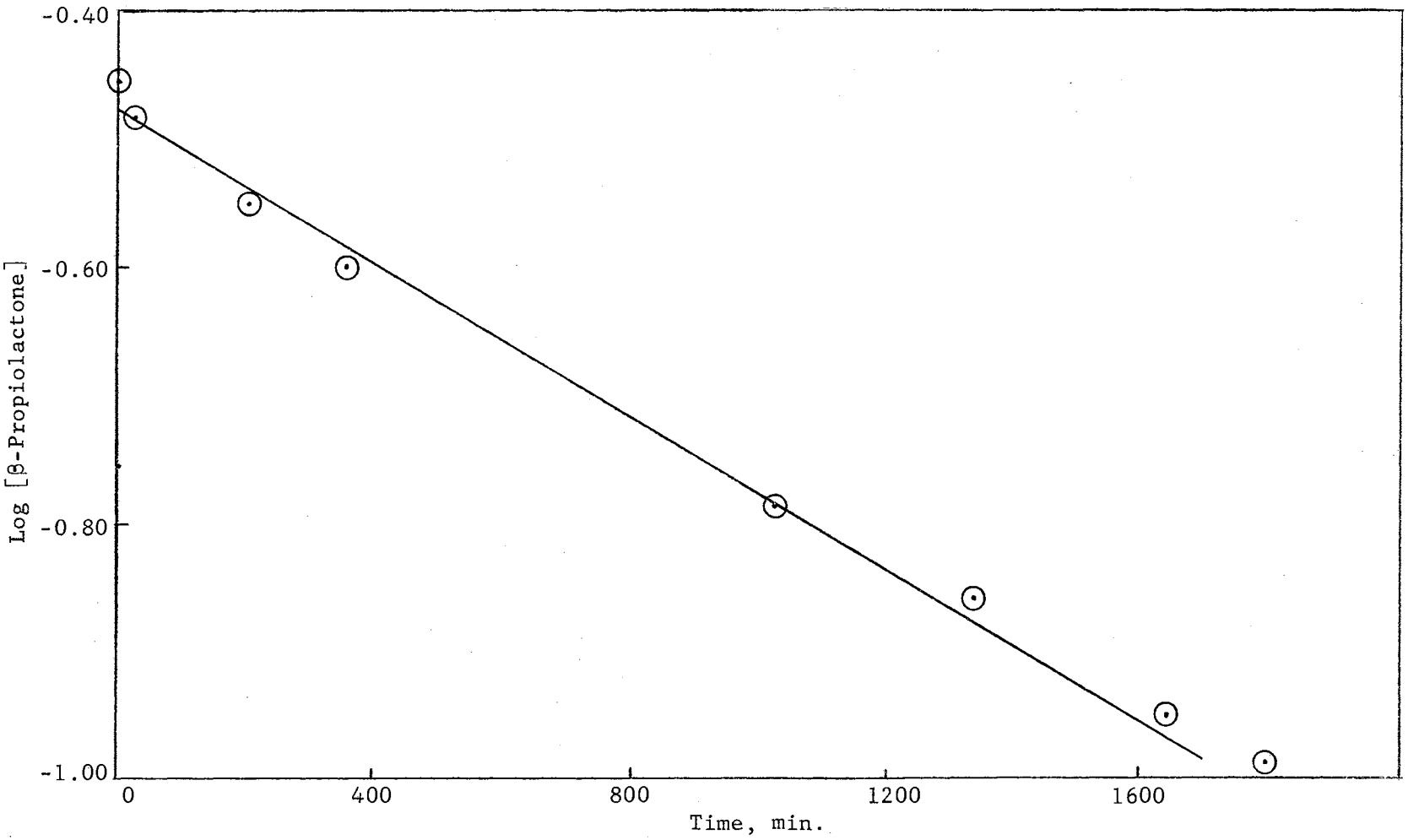


Figure 5. First-Order Plot for the Base-Catalyzed Homopolymerization of β-Propiolactone at 55^{o} in Acetonitrile.

condenser and stirrer. Diethylamine initiator (4.00 ml., 0.088 N) in dioxane was added to the flask as the stop watch was started. The change in concentration of β-propiolactone was determined as previously described. The data obtained are presented in Table VI.

The data are also plotted as a pseudo first-order reaction in Figure 6. The slope of the line of Figure 6 is -2.6×10^{-3}. The rate constant for the pseudo first-order reaction is: $k_{55^o} = 6.0 \times 10^{-3}$ min.$^{-1}$

TABLE VI

RATE OF BASE-CATALYZED HOMOPOLYMERIZATION OF β-PROPIOLACTONE AT 55° IN DIMETHYL SULFOXIDE

Time, minutes	Concentration of unreacted β-propiolactone, eq./l.
3.5	0.1297
13.5	0.1195
27	0.1152
48	0.1027
72	0.0905
180	0.0477
225	0.0321

Homopolymerization of DL-Valine-NCA. The rate of polymerization of NCA's can be determined by measuring the amount of CO_2 evolved. This may be accomplished by transferring the CO_2, with N_2, into a solution of benzylamine in benzene and ethanol. The carbamic acid derivative

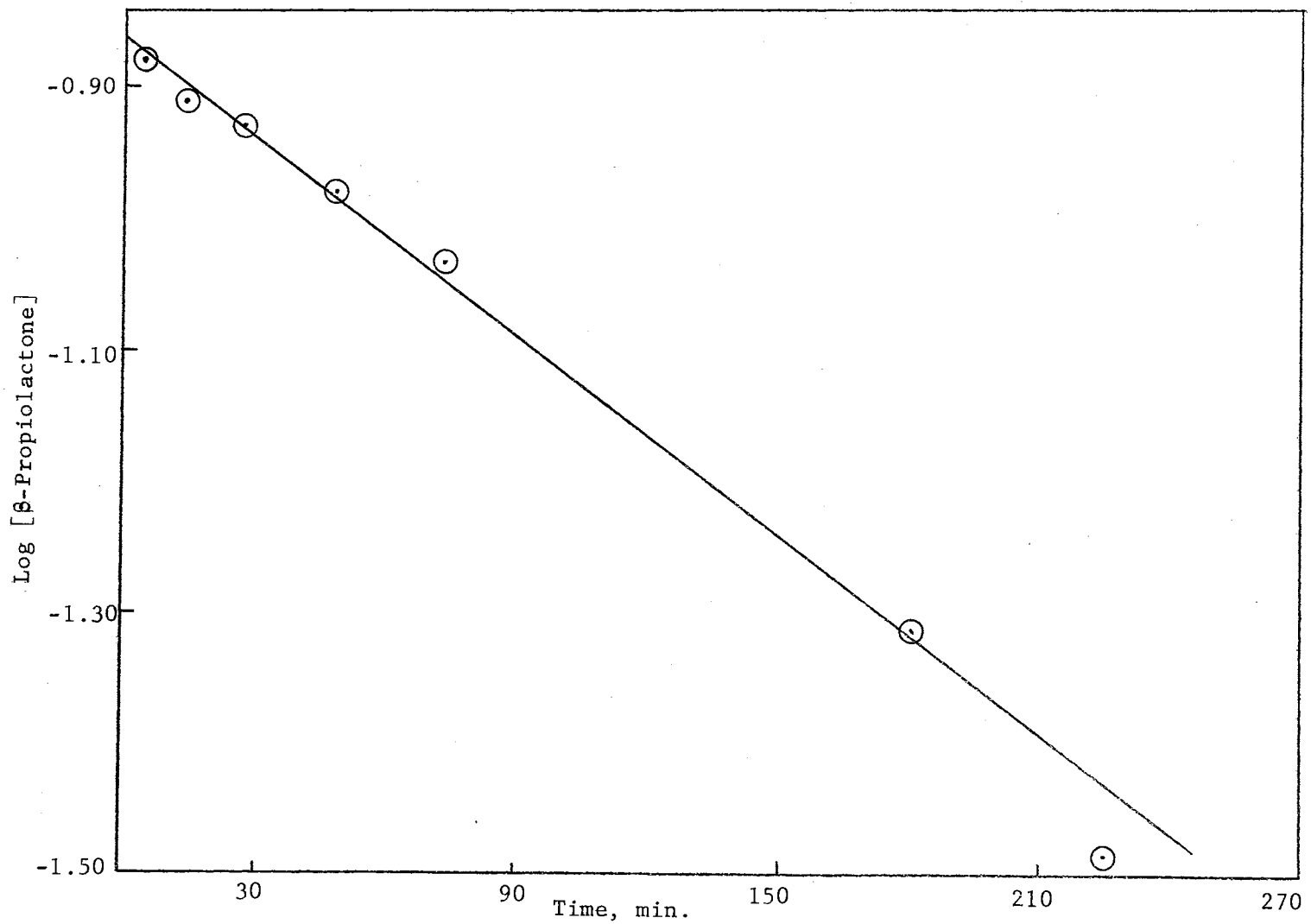


Figure 6. First-Order Plot for the Base-Catalyzed Homopolymerization of β-Propiolactone at 55° in Dimethyl Sulfoxide.

formed is titrated with standard $NaOCH_3$ to the blue end-point of thymol-blue indicator (162).

DL-Valine-NCA (3.00 g., 0.021 mole) was added to acetonitrile (400 ml.) in a 3-neck, 500-ml., round-bottom flask. The flask was fitted with a gas-dispersion inlet tube, a mercury-seal stirrer, and a Friedrichs condenser. The apparatus was assembled in a constant-temperature bath at 55°. Nitrogen gas was bubbled through concentrated NaOH solution, two Ascarite tubes, and a $CaCl_2$ drying-tube into the reaction vessel. The apparatus was designed so the gases could leave the flask through the condenser and pass into a solution of benzylamine in benzene. All connections on the apparatus were sealed with glyptal resin to prevent loss of CO_2.

After thermal equilibrium was established 0.088 N diethylamine (11.00 ml., 0.968 millimole) in dioxane was added, and the stop watch was started. At known times the flow of N_2 into the reaction vessel was stopped, and the carbamic acid derivative was titrated with 0.1400 N $NaOCH_3$ in benzene-methanol solution. The data obtained are presented in Table VII and plotted in Figure 7.

The polymer precipitated during the reaction, and although a straight line was obtained in Figure 7, attempts to reproduce the data were not successful.

The kinetic study was also attempted in anisole, dimethyl sulfoxide, and dimethyl sulfoxide-anisole. In each trial the polypeptide precipitated.

TABLE VII

RATE OF BASE-CATALYZED HOMOPOLYMERIZATION OF DL-VALINE-NCA AT 55° IN ACETONITRILE

Time, minutes	Concentration of unreacted NCA, eq./l.
9	0.0517
13	0.0507
22	0.0486
54	0.0403
106	0.0344
139	0.0308
169	0.0293

Attempted Homopolymerization of Propylene Oxide. Propylene oxide (10 ml.), which had been dried over pellet KOH and distilled, was added to anhydrous ether (25 ml.) in a 50-ml. round-bottom flask. A solution (1.00 ml.) of n-butyllithium in ether was added to the flask, and a white precipitate formed. Since the reaction was heterogeneous, kinetic studies were not attempted.

A 0.2644 N solution of propylene oxide in CH_2Cl_2 was prepared in a 50-ml. volumetric flask. Two aliquots (3.00 ml.) were withdrawn and transferred to a measured excess of dioxane·HCl reagent (117). A few drops of triethylamine initiator were added, and aliquots (3.00 ml.) were transferred to dioxane·HCl, 1 and 3.5 hours later. The excess acid was titrated with standard methanolic sodium hydroxide. The concentration of propylene oxide did not change significantly over a 3.5-hour period.

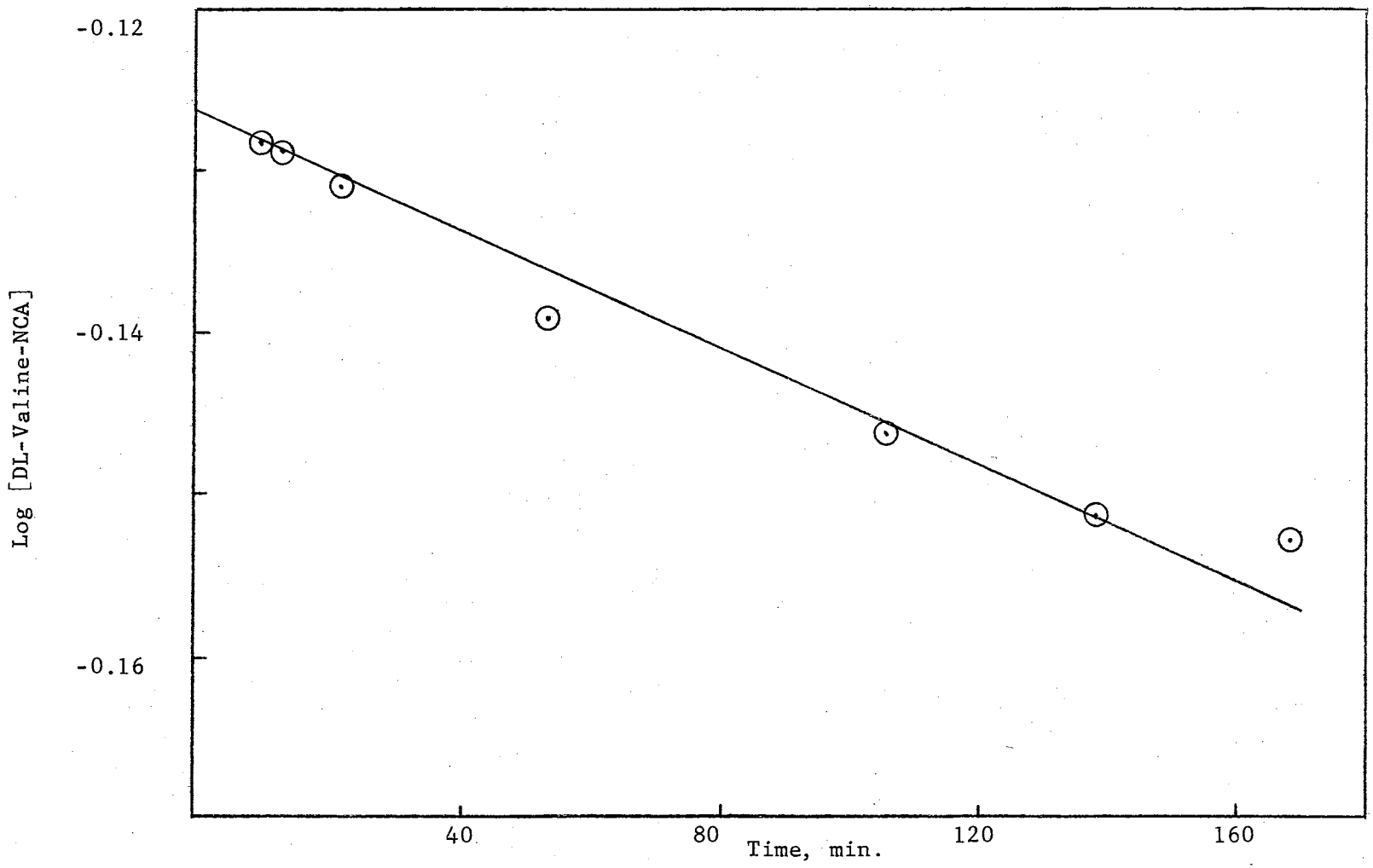


Figure 7. First-Order Plot for the Base-Catalyzed Homopolymerization of DL-Valine-NCA.

Propylene oxide (1.6 g., 0.02 mole) was dissolved in $CHCl_3$ (25 ml.). 1,4-Diazabicyclo[2.2.2.]octane initiator (0.3 g., 0.003 mole) was added to the flask and dissolved. An aliquot (2.00 ml.) of the solution was added to dioxane·HBr solution (15.00 ml.). Another aliquot (2.00 ml.) was taken the following day and also added to dioxane·HBr (15.00 ml.). The excess acid in each sample was titrated with standard methanolic sodium hydroxide. Each sample required 1.10 ml. of base, indicating that the concentration of propylene oxide monomer did not change overnight.

Several other bases were examined as possible catalysts for the homogeneous polymerization of propylene oxide in various solvents. Excess $LiOC_2H_4OC_2H_5$ was added to toluene, dioxane, CCl_4, anisole, nitrobenzene, $CHCl_3$, dimethyl ether of triethylene glycol, N,N-dimethylformamide, ether, and formamide. The base was shown to be essentially insoluble in these solvents by removing the excess by filtration, hydrolyzing the base, if any, in solution and determining the pH with pH indicator. The same procedure was repeated with $KOC(CH_3)_3$, $LiOC(CH_3)_3$, and $LiOCH_3$ in boiling N,N-dimethylformamide, and also with cetyldimethylethylammonium isopropoxide in N,N-dimethylformamide at 60°. After the excess base was removed, the base in solution was hydrolyzed and the solution allowed to cool to room temperature. Phenolphthalein turned slightly pink in the solutions of the potassium salt and the quaternary ammonium base. The pH of the potassium salt solution was not greater than 10. The lithium salt solution remained colorless in the presence of phenolphthalein. None of the bases tested were sufficiently soluble to serve as homogeneous polymerization catalysts.

Attempted Homopolymerization of the β-Lactone of 2,2,4-Trimethyl-3-Hydroxy-3-Pentenoic Acid (TMBL). TMBL (23 g., 0.16 mole) was slowly added from an addition funnel to a solution of acetonitrile (200 ml.) containing a catalytic amount of trimethylphenylammonium methoxide in a 3-neck, 500-ml., round-bottom flask fitted with a stirrer, an addition funnel, and a reflux condenser. Nitrogen was passed over the surface of the solution and reflux was maintained during the reaction. The contents of the flask gradually became golden-yellow. After 23 hours the reaction was stopped. A portion of the reaction mixture was poured into rapidly stirred ether, but precipitation did not occur. Monomer was recovered by removal of the solvent. Attempts to polymerize TMBL with triethylamine were also unsuccessful.

Acid-Catalyzed Polymerizations

Homopolymerization of Propylene Oxide. The procedure used to determine the concentration of unreacted propylene oxide was a method (117) shown to be applicable to both water-soluble and water-insoluble epoxides. The procedure measures the amount of acid consumed by the epoxide. The ring-opening reagent is a 0.2 N solution of concentrated HCl in dioxane. The epoxide is added to excess dioxane·HCl reagent, allowed to react for at least 15 minutes, and the excess acid is back-titrated to the purple end-point of cresol-red indicator in neutralized ethanol.

Freshly distilled propylene oxide (3.00 ml.) which had been dried over pellet KOH was transferred to a 200-ml. volumetric flask. The flask was diluted to volume with CH_2Cl_2 at 27.0°. An aliquot (5.00 ml.) of the solution was transferred to a 250-ml. Erlenmeyer flask containing

dioxane·HCl reagent (15.00 ml.).

A 0.57 N solution of BF_3 etherate catalyst (2.00 ml., 1.14 milliequivalents) in CH_2Cl_2 and 1.48 N methanol co-catalyst (1.00 ml., 1.48 milliequivalents) in CH_2Cl_2 were added to the volumetric flask from pipettes as the stop watch was started. The change in concentration of propylene oxide with time was determined by transferring aliquots (5.00 ml.) of the solution to flasks containing dioxane·HCl (15.00 ml.). The flasks were protected against moisture and after 15 minutes the contents were diluted with neutralized ethanol (15.00 ml.) containing cresol-red indicator. The excess acid was titrated with 0.5707 N methanolic sodium hydroxide.

A blank was prepared by adding 0.57 N BF_3 etherate (0.20 ml., 0.114 milliequivalents) and 1.48 N methanol (0.10 ml., 0.148 milliequivalents) to CH_2Cl_2 (20.00 ml.). An aliquot (5.00 ml.) was reacted with dioxane·HCl (15.00 ml.). After 15 minutes the solution was diluted with neutralized ethanol and titrated with the same standard sodium hydroxide. The titrations were performed with a micro-burette the contents of which were protected from atmospheric CO_2 by an Ascarite tube. The burette was filled with base by N_2 pressure so that the base was never exposed to atmospheric CO_2.

The data obtained are presented in Table VIII and plotted as a pseudo first-order reaction in Figure 8. The experimental points of Figure 8 indicate that the reaction is more complex than pseudo first order. Propylene oxide forms the corresponding 1,4-dioxane when treated with acid. This may explain the observed deviation from simple pseudo first-order kinetics.

The change in concentration of propylene oxide reacted as a

function of time is plotted in Figure 10.

TABLE VIII

RATE OF ACID-CATALYZED HOMOPOLYMERIZATION OF PROPYLENE OXIDE AT 27° IN METHYLENE CHLORIDE

Time, minutes	Concentration of unreacted epoxide, eq./l.
0	0.2281[a]
1.5	0.1666
36	0.0833
57	0.0650
79	0.0570
106	0.0514

[a]The sample at t = 0 was withdrawn before the catalyst was added. This value is corrected for volume dilution from 200 to 203 ml.

Homopolymerization of Epichlorohydrin. Freshly distilled epichlorohydrin (3.00 ml.) was transferred to a 200-ml. volumetric flask and was diluted to volume with CH_2Cl_2 at 27.0°. An aliquot (5.00 ml.) of the solution was transferred to a flask containing dioxane·HCl reagent (15.00 ml.).

A 0.57 N solution of BF_3 etherate catalyst (2.00 ml., 1.14 milliequivalents) in CH_2Cl_2 and 1.48 N methanol co-catalyst (1.00 ml., 1.48 milliequivalents) in CH_2Cl_2 were added to the volumetric flask from pipettes as the stop watch was started. The change in concentration of epichlorohydrin was determined as previously described for propylene oxide.

The data obtained are presented in Table IX and plotted as a

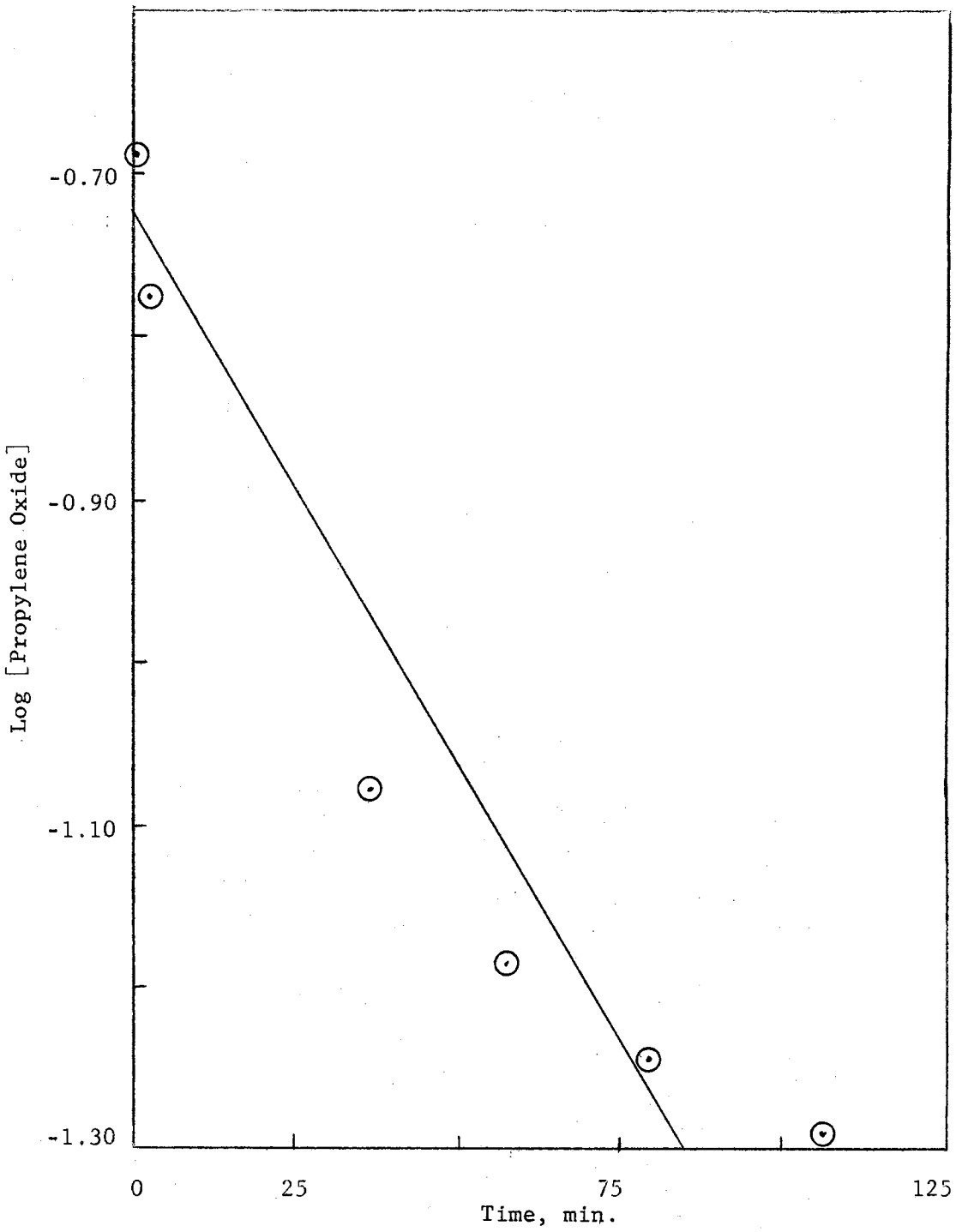


Figure 8. First-Order Plot for the Acid-Catalyzed Homopolymerization of Propylene Oxide.

as a pseudo first-order reaction in Figure 9. The slope of the line of Figure 9 is -4.2×10^{-3}. The rate constant of the pseudo first-order reaction is 9.7×10^{-3} min.$^{-1}$

The change in concentration of epichlorohydrin reacted as a function of time is plotted in Figure 10.

TABLE IX

RATE OF ACID-CATALYZED HOMOPOLYMERIZATION OF EPICHLOROHYDRIN AT 27° IN METHYLENE CHLORIDE

Time, minutes	Concentration of unreacted epoxide, eq./l.
0	0.2114[a]
1.5	0.1975
13	0.1803
36	0.1427
53	0.1244
85	0.0947
141	0.0514

[a]The sample at t = 0 was withdrawn before the catalyst was added. This value is corrected for volume dilution from 200 to 203 ml.

Copolymerization of Epichlorohydrin and Propylene Oxide.

Epichlorohydrin (3.00 ml.) and propylene oxide (3.00 ml.) were transferred to a 200-ml. volumetric flask which was diluted to volume with CH_2Cl_2 at 27.0°. An aliquot (5.00 ml.) was transferred to a flask containing dioxane·HCl reagent (15.00 ml.).

BF_3 etherate catalyst and methanol co-catalyst were added just as before.

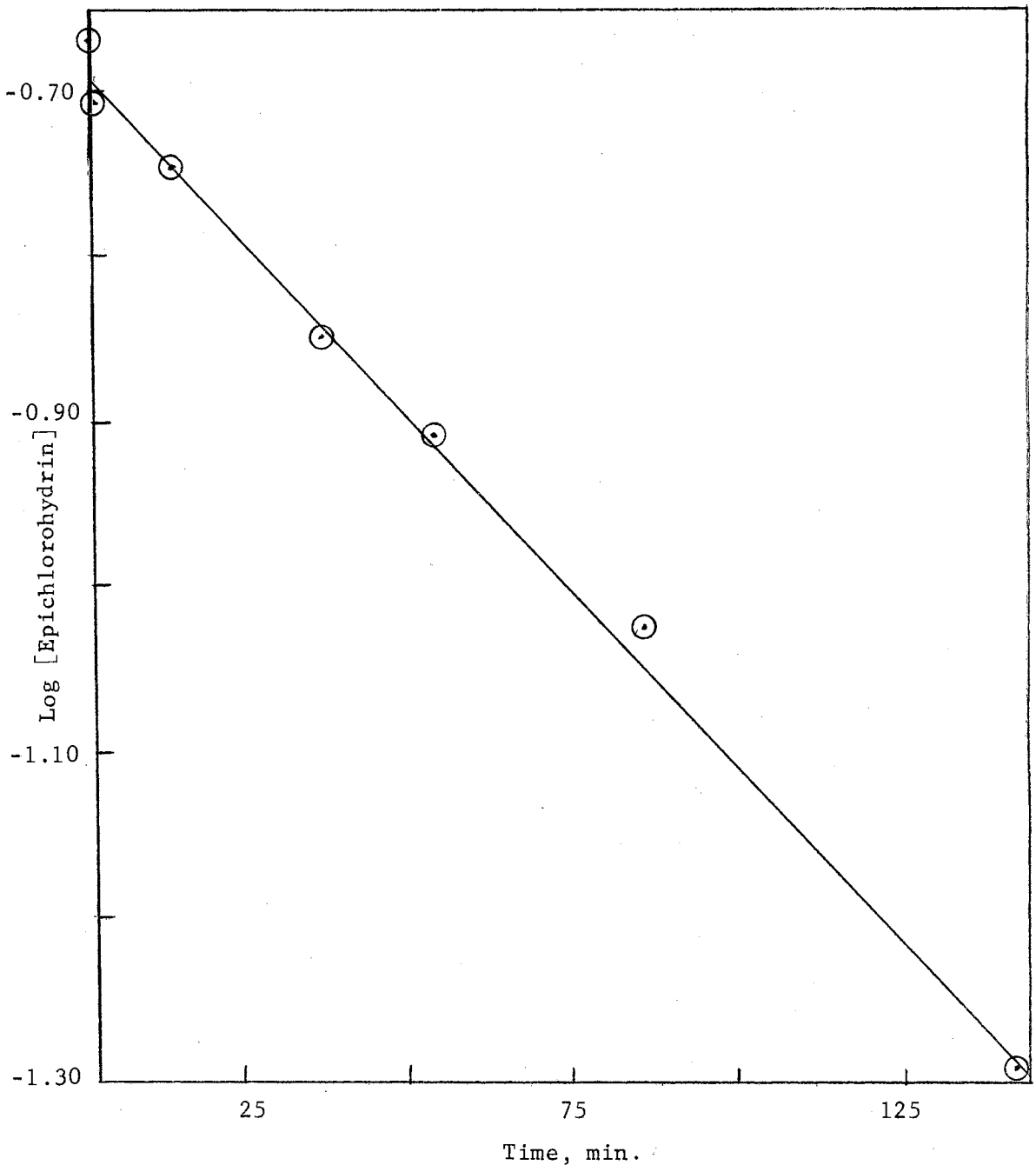


Figure 9. First-Order Plot for the Acid-Catalyzed Homopolymerization of Epichlorohydrin.

The change in concentration of epoxides was determined as previously described for propylene oxide. The data obtained are presented in Table X. The change in concentration of epoxide reacted as a function of time is plotted in Figure 10.

TABLE X

RATE OF ACID-CATALYZED COPOLYMERIZATION OF PROPYLENE OXIDE AND EPICHLOROHYDRIN AT 27° IN METHYLENE CHLORIDE

Time, minutes	Concentration of unreacted epoxides, eq./l.
0	0.4178[a]
1.5	0.3566
13	0.2877
38	0.2484
79	0.2189
120	0.2016

[a]The first sample was withdrawn before catalyst was added. This value is corrected for volume dilution from 200 to 203 ml.

Homopolymerization of Propylene Sulfide. Acetyl chloride reacts quantitatively with propylene sulfide (44). A procedure was developed for the quantitative determination of propylene sulfide based upon this reaction.

The reagent was prepared by adding acetyl chloride (6 g., 0.08 mole) and a catalytic amount of BF_3 etherate to toluene (200 ml.).

Propylene sulfide (0.9684 g., 0.013 mole) was diluted to volume with CH_2Cl_2 in a 50-ml. volumetric flask. The concentration of the solution was 0.2612 N. Aliquots (3.00 ml.) of the propylene sulfide

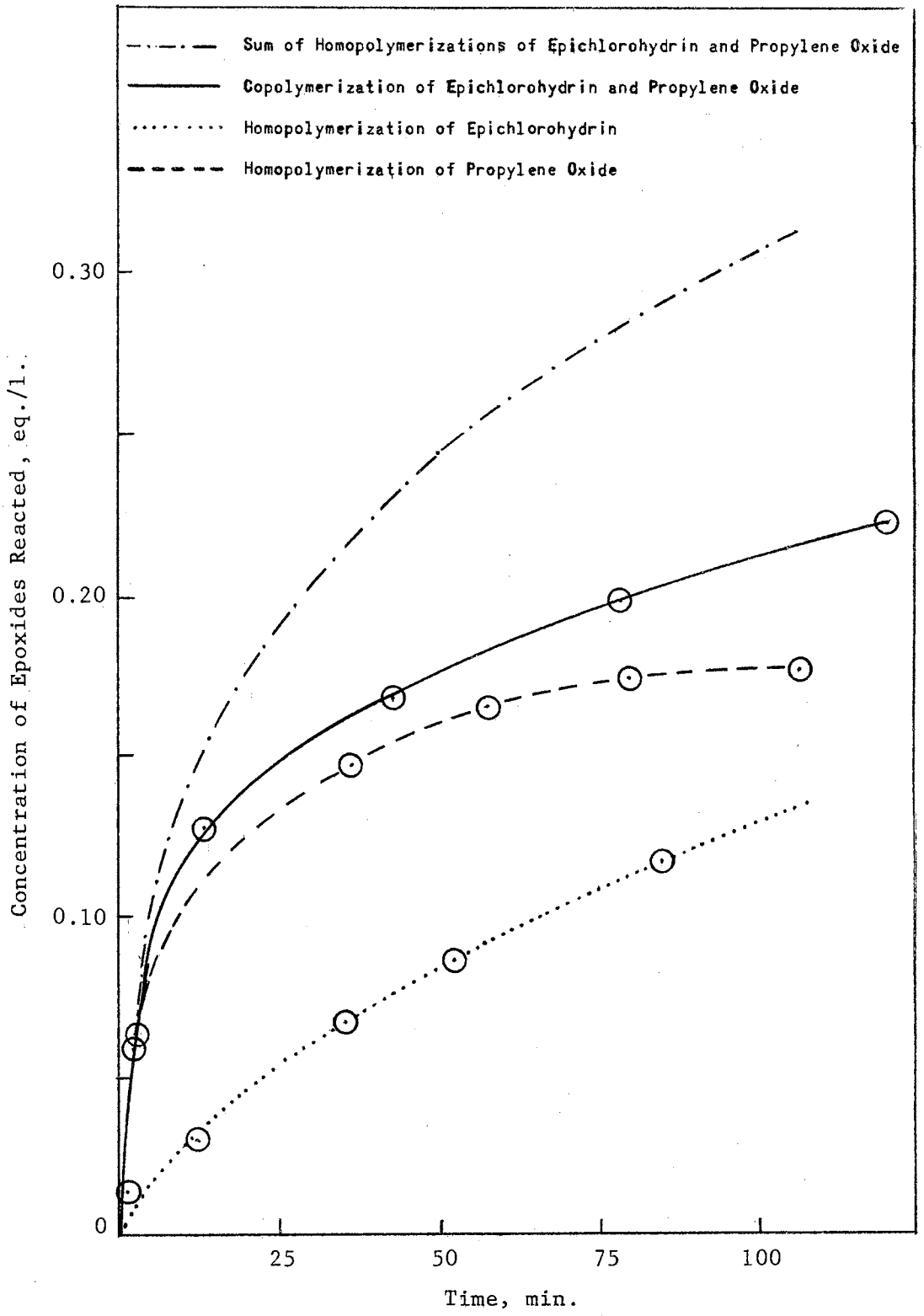


Figure 10. Concentration of Monomer Reacted as a Function of Time for the Homopolymerizations and Copolymerization of Propylene Oxide and Epichlorohydrin.

solution were added to aliquots of the reagent (5.00 ml.). The excess acetyl chloride was titrated with a 0.1400 N solution of $NaOCH_3$ in 3 parts methanol and 1 part benzene (73a). The samples were titrated to the yellow end-point of thymol-blue indicator. An aliquot (5.00 ml.) of the acetyl chloride reagent was also titrated with the base to the same end-point. The difference in the amount of base consumed by the blank and by the sample is equivalent to the amount of propylene sulfide present in the sample. Samples should react for at least 8 hours before titrations are performed. A sample allowed to react for 8 hours gave 95 per cent of theoretical and when reaction time was extended to 2 days gave 104 per cent. The procedure is suitable for kinetic studies and was used for this purpose.

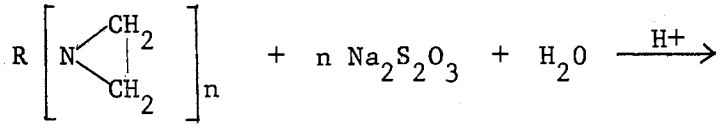
Dry, freshly distilled propylene sulfide (3.00 ml.) was diluted to volume with CH_2Cl_2 at 30° in a 200-ml. volumetric flask. An aliquot (5.00 ml.) was added to the acetyl chloride reagent (10.00 ml.). A 0.57 N solution of BF_3 etherate catalyst (2.00 ml., 1.14 milliequivalents) in CH_2Cl_2 and 1.48 N methanol co-catalyst (1.00 ml., 1.48 milliequivalents) in CH_2Cl_2 were added to the volumetric flask as the stop watch was started. The change in concentration of propylene sulfide was determined by transferring aliquots (5.00 ml.) of the solution to aliquots (10.00 ml.) of the acetyl chloride reagent. The data obtained are presented in Table XI and plotted as a pseudo first-order reaction in Figure 11. Polymer precipitated upon addition of catalyst. Since the reaction was obviously not pseudo first order, a reaction rate constant was not determined.

TABLE XI

RATE OF ACID-CATALYZED HOMOPOLYMERIZATION OF PROPYLENE SULFIDE AT 30° IN METHYLENE CHLORIDE

Time, minutes	Concentration of unreacted propylene sulfide, eq./l.
0	0.2209
2	0.1439
19	0.1005
30	0.0952
72	0.0918

Homopolymerization of N-(2-Hydroxyethyl)aziridine. A procedure for the quantitative estimation of aziridines furnished by the Texas Division of the Dow Chemical Company was used with only minor modifications for the determination of N-(2-hydroxyethyl)aziridine (NHEA) and N-(2-hydroxy-n-propyl)aziridine (NHPA). The procedure is based upon the following reaction:



$$R(NCH_2CH_2S_2O_3^- \; Na^+)n \; + \; n \; NaOH$$

The reaction is conducted in excess $Na_2S_2O_3$ solution in the presence of acid. The NaOH formed is neutralized by the excess acid present. Back-titration of the excess acid determines the net amount of acid used to neutralize the sodium hydroxide, and, therefore, gives the amount of aziridine present. The change in concentration of NHEA was followed by transferring an aliquot (3.00 ml.) of the solution into a flask

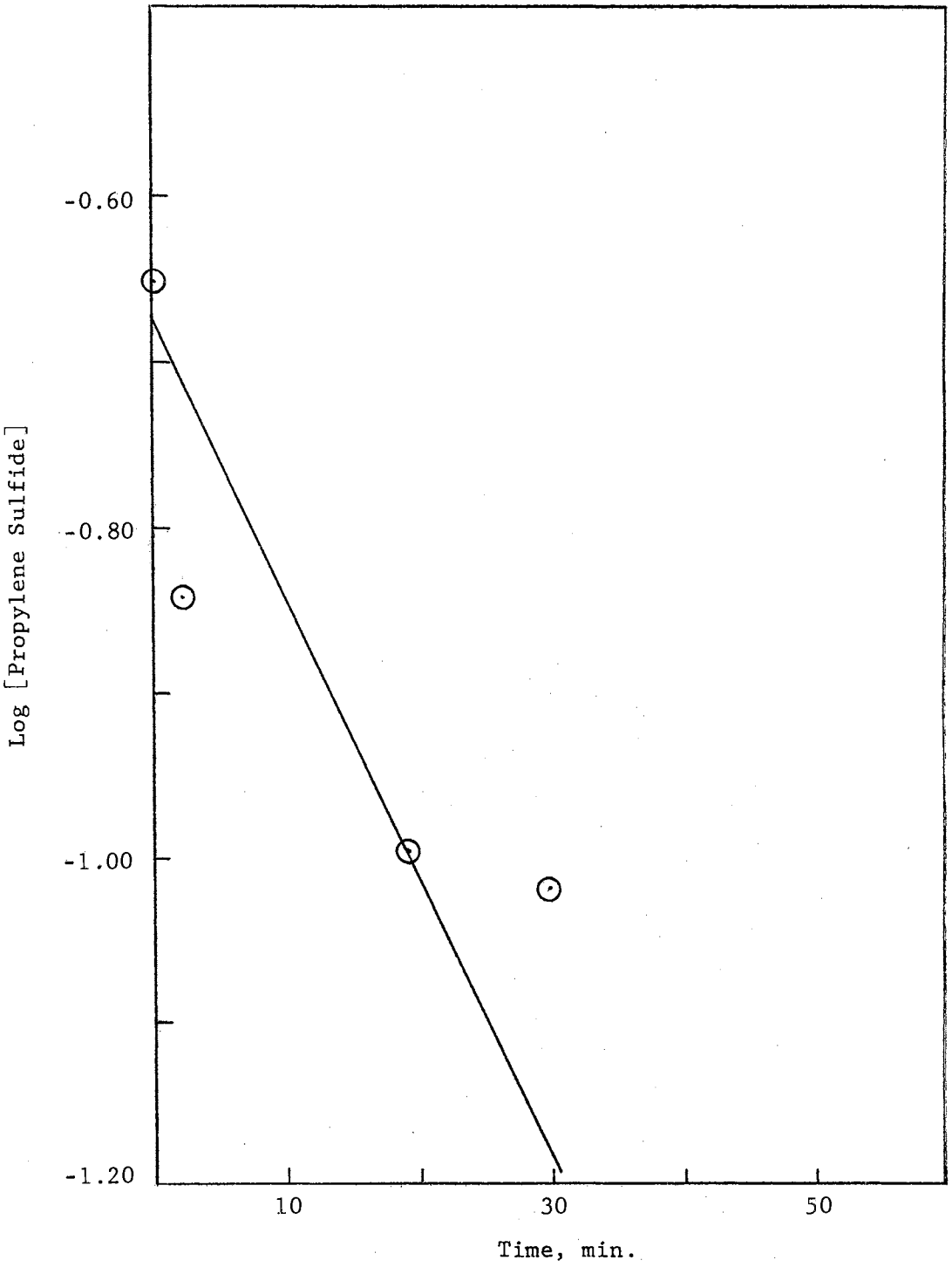


Figure 11. First-Order Plot for the Acid-Catalyzed Homopolymerization of Propylene Sulfide.

containing 20 per cent $Na_2S_2O_3$ solution (50.00 ml.). The solution was titrated to pH 4 with 0.1 N H_2SO_4. As the base was formed the pH began to increase. An additional quantity of acid was added to maintain pH 4. A blank of the 20 per cent $Na_2S_2O_3$ solution (50 ml.) was also titrated to pH 4. The blank was found to be insignificant, however, so its use was discontinued in the kinetic studies. The blank and the sample were set aside for 30 minutes and were back-titrated with 0.1 N sodium hydroxide. The end-point was determined by potentiometric titration using a Beckman Model 72 pH meter. The end-point for NHEA was found to be pH 9.75 and for NHPA was pH 9.70. In the kinetic investigation of NHEA and NHPA a potentiometric titration was performed for each sample rather than titrating to a definite pH. The difference between the milliequivalents of acid and base used, divided by the size of the aliquot taken, gave the concentration of unreacted aziridine.

NHEA (2.9313 g., 0.034 mole) was weighed in a 25-ml. volumetric flask, and was diluted with distilled H_2O (14.50 ml.). The flask was placed in a constant-temperature bath at 30.0°. After thermal equilibrium was established, 0.1069 N H_2SO_4 (7.50 ml., 0.8 milliequivalent) was added as the stop watch was started. Less than 1.00 ml. of additional H_2O was required to dilute to volume.

The change in concentration of NHEA was determined by withdrawing aliquots (3.00 ml.) and transferring these to flasks containing 20 per cent $Na_2S_2O_3$ solution. The pH was adjusted to 4 by addition of 0.1011 N H_2SO_4. The acid was back-titrated with 0.1087 N NaOH solution. The end-point was determined by potentiometric titration. The data obtained are presented in Table XII and are plotted as a pseudo first-order reaction in Figure 12. The results show the reaction to be

more complex than pseudo first order. The concentration of monomer reacted as a function of time is plotted in Figure 14.

TABLE XII

RATE OF ACID-CATALYZED HOMOPOLYMERIZATION OF N-(2-HYDROXYETHYL)AZIRIDINE AT 30° IN DILUTE SULFURIC ACID

Time, minutes	Concentration of unreacted NHEA, eq./l.
2	1.1654
12	0.6704
22	0.4900
36	0.4622

Homopolymerization of N-(2-Hydroxy-n-propyl)aziridine. N-(2-Hydroxy-n-propyl)aziridine (NHPA) was polymerized with the same amount of catalyst and solvent used for NHEA. The weight of NHPA used was 2.7637 g. (0.027 mole).

The change in concentration of NHPA was determined by the procedure previously described for NHEA. The data obtained are presented in Table XIII and are plotted as a pseudo first-order reaction in Figure 13. The acid-catalyzed homopolymerization of NHPA is also more complex than pseudo first order. The concentration of NHPA reacted as a function of time is plotted in Figure 14.

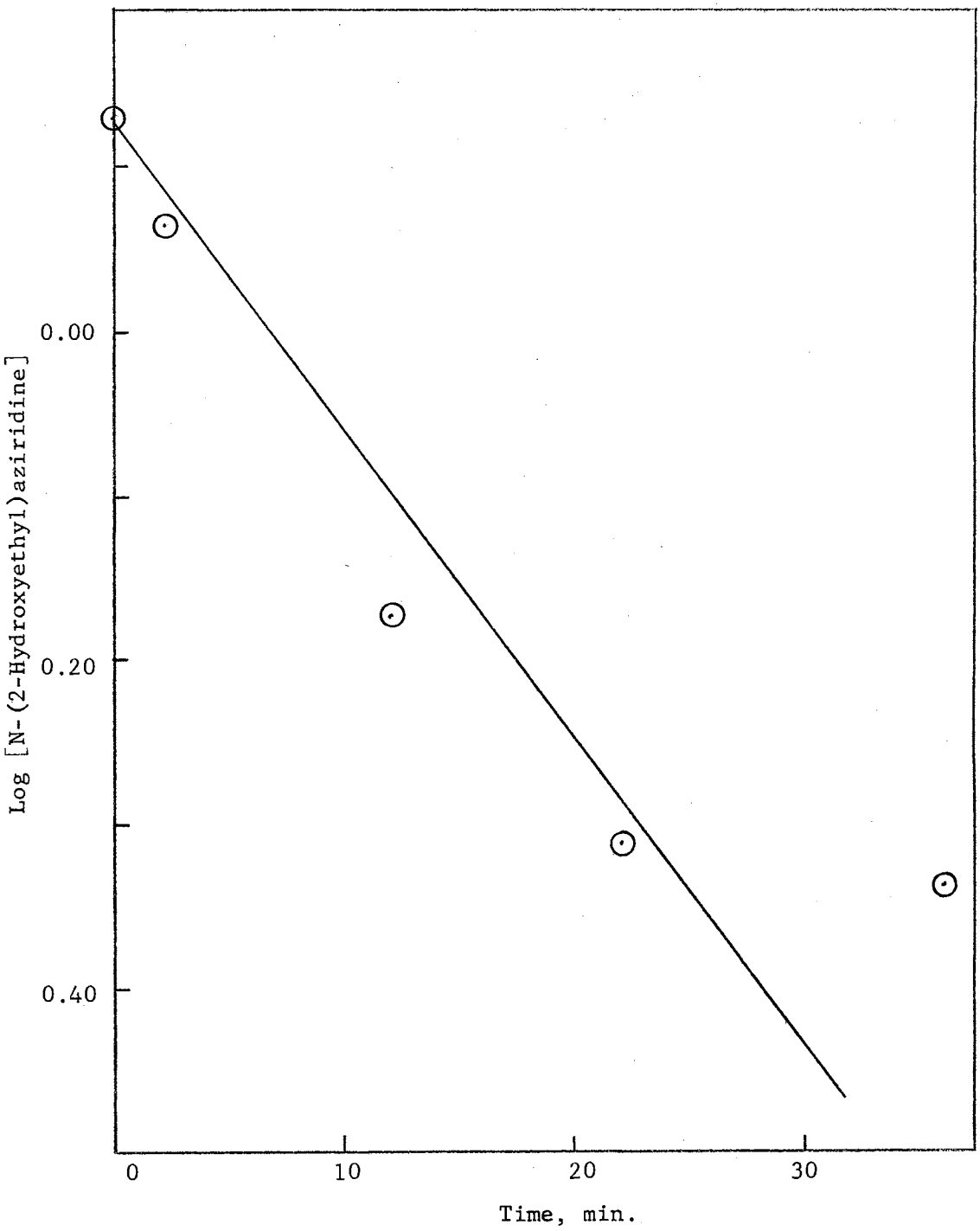


Figure 12. First-Order Plot for the Acid-Catalyzed Homopolymerization of N-(2-Hydroxyethyl)aziridine.

TABLE XIII

RATE OF ACID-CATALYZED HOMOPOLYMERIZATION OF N-(2-HYDROXY-n-PROPYL)AZIRIDINE AT 30° IN DILUTE SULFURIC ACID

Time, minutes	Concentration of unreacted NHPA, eq./l.
3	0.9879
14	0.6551
28	0.5020
38	0.4743

Copolymerization of N-(2-Hydroxyethyl)aziridine and N-(2-Hydroxy-n-propyl)aziridine. NHEA (5.7500 g., 0.066 mole) and NHPA (5.5700 g., 0.055 mole) were weighed in a 50-ml. volumetric flask. The contents of the flask were diluted with distilled H_2O (29.00 ml.) at 30°. The volumetric flask was placed in a constant-temperature bath at 30° and 0.1069 N H_2SO_4 (15.00 ml., 0.16 milliequivalents) was added as the stop watch was started. A small additional quantity of distilled H_2O was added to dilute the solution to volume. The change in concentration of total aziridine monomers was determined as previously described for NHEA and NHPA using aliquots (3.00 ml.) of the solution. However, in this investigation 100 ml. of 20 per cent $Na_2S_2O_3$ solution was used rather than 50 ml. as in the homopolymerization reactions. The data obtained are presented in Table XIV. The concentration of monomer reacted as a function of time is plotted in Figure 14.

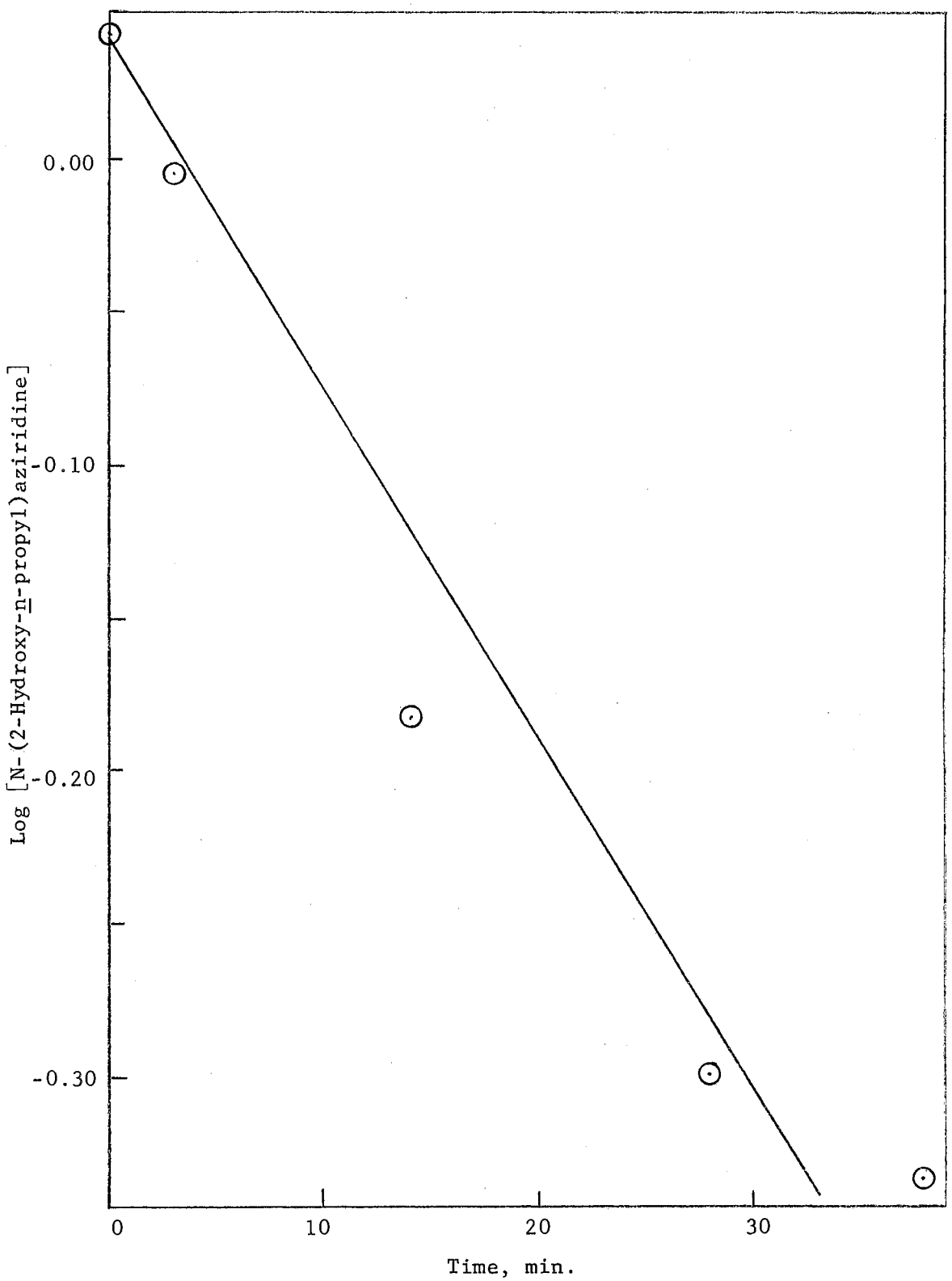


Figure 13. First-Order Plot for the Acid-Catalyzed Homopolymerization of N-(2-Hydroxy-n-propyl)aziridine.

TABLE XIV

RATE OF ACID-CATALYZED COPOLYMERIZATION OF N-(2-HYDROXYETHYL)AZIRIDINE AND N-(2-HYDROXY-n-PROPYL)AZIRIDINE AT 30° IN DILUTE SULFURIC ACID

Time, minutes	Concentration of unreacted aziridine, eq./l.
3	1.8859
16	1.1967
27	1.0528
39	0.9847

Homopolymerization of 3,3-bis(Chloromethyl)oxetane. Before kinetic studies could be undertaken with 3,3-bis(chloromethyl)oxetane (BCMO) it was necessary to develop a reliable procedure for the determination of this monomer. The procedure used for the determination of epoxides was found to be satisfactory.

Aliquots of a 0.1651 N solution of BCMO in $CHCl_3$ were analyzed as previously described for propylene oxide. However, the ring-opening reagent used was dioxane·HBr, and reaction time was extended to 8 hours before the excess acid was back-titrated with standard base. The experimentally determined concentration of BCMO was 0.1608 N. Thus the method is suitable for kinetic studies.

An attempt to study the kinetics of homopolymerization of BCMO at 30° was unsuccessful. The concentration of monomer did not change over a one-hour period.

An attempt to study the kinetics in a solution of equal volumes of BCMO and $CHCl_3$ at 30°, using BF_3 initiator, also was unsuccessful. The

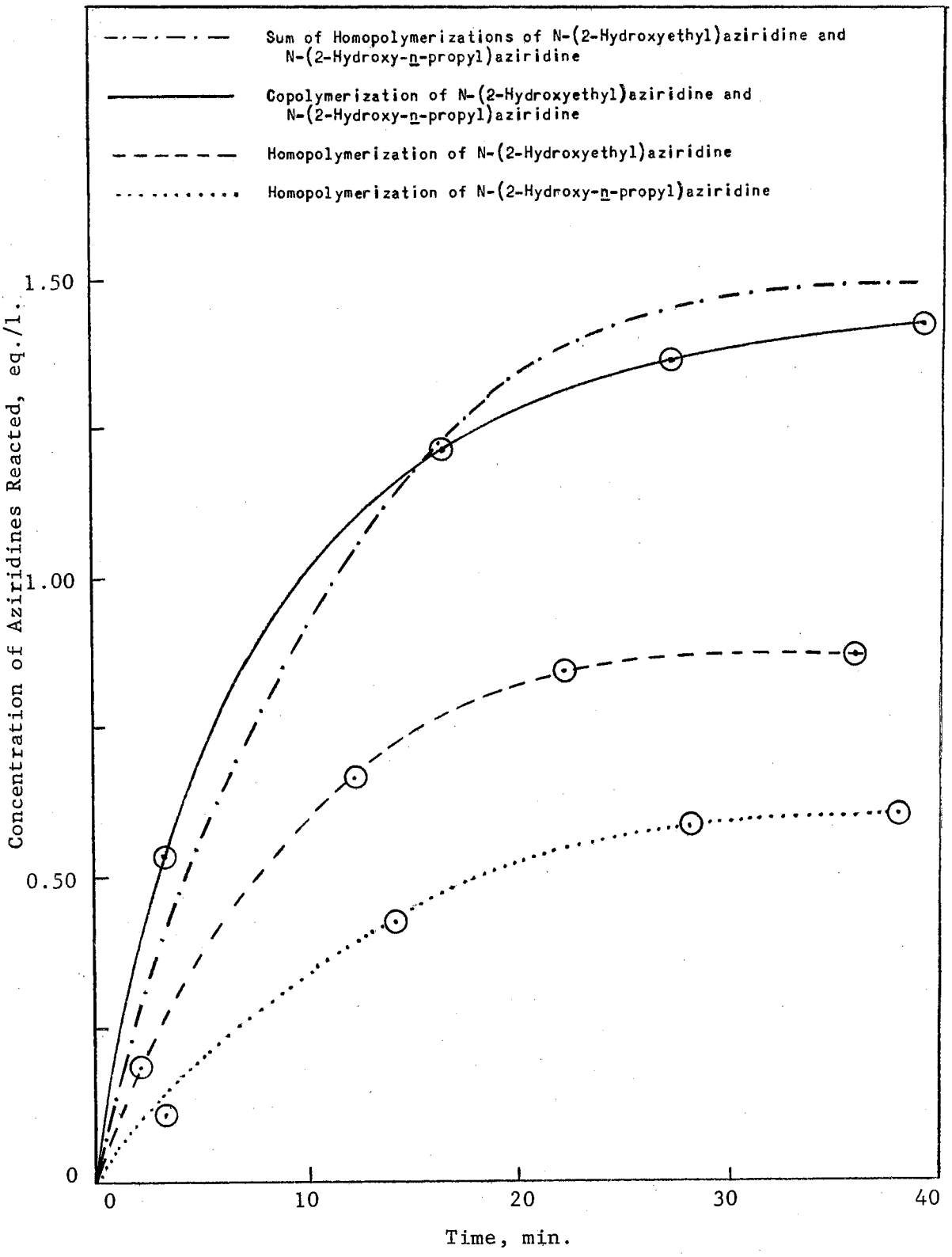


Figure 14. Concentration of Monomers Reacted as a Function of Time for the Homopolymerizations and Copolymerization of N-(2-Hydroxyethyl)aziridine and N-(2-Hydroxy-n-propyl)aziridine.

monomer concentration did not change during the first 20 minutes. After this time the concentration of BCMO did decrease, but the polymer precipitated. Since the reaction had become heterogeneous, kinetic studies were discontinued.

BCMO was polymerized to 75 per cent conversion in o-dichlorobenzene at 100°. This temperature was maintained by inserting a reaction tube of approximately 25-ml. capacity into a 3 l., 3-neck, round-bottom flask. The flask was fitted with a reflux condenser and approximately 1 l. of H_2O was added. The H_2O was heated to boiling and the vapor allowed to condense on the reaction tube. The flask was wrapped with glass wool and foil. The reaction tube was fitted with a Friedrichs condenser.

BCMO (1.00 ml.) and o-dichlorobenzene (10.00 ml.) were added to the reaction tube from pipettes. After thermal equilibrium was established 12.45 per cent BF_3 etherate (0.25 ml.) was added from a 250-λ pipette as the stop watch was started. The reaction was followed by transferring aliquots (2.00 ml.) of the solution to flasks containing dioxane·HBr (20.00 ml.).

A blank was prepared by adding o-dichlorobenzene (11.00 ml.) and 12.45 per cent BF_3 etherate (0.25 ml.) to the reaction tube. After thermal equilibrium was established an aliquot (2.00 ml.) of the blank was transferred to dioxane·HBr (20.00 ml.). After one day, the samples and blank were diluted with neutralized ethanol (20.00 ml.) containing cresol-red indicator and the excess acid was back-titrated with 0.5548 N methanolic sodium hydroxide. The data obtained are presented in Table XV and plotted as a pseudo second-order reaction in Figure 15. The rate constant is 2.5×10^{-2} l. mole^{-1} min.$^{-1}$

TABLE XV

RATE OF ACID-CATALYZED HOMOPOLYMERIZATION OF 3,3-BIS(CHLOROMETHYL)OXETANE AT 100° IN o-DICHLOROBENZENE

Time, minutes	Concentration of unreacted BCMO, eq./l.
5	0.5853
25	0.3800
62	0.2524
122	0.1914
177	0.1553

Attempted Homopolymerization of 3,3-bis(Iodomethyl)oxetane. A kinetic investigation of the homopolymerization of 3,3-bis(iodomethyl)-oxetane (BIMO) was attempted. BIMO (2.0004 g., 0.006 mole) was dissolved in o-dichlorobenzene (10.00 ml.) at room temperature. The constant-temperature apparatus previously described for BCMO was used. When 12.45 per cent BF_3 etherate (0.25 ml.) was added, a precipitate formed immediately. The kinetic study was discontinued since the reaction had become heterogeneous. After 30 minutes, the product was isolated by filtration and washed with acetone. The product was a fine white powder; m.p. 252-255°. The melting point of the monomer is 50°; therefore starting material was not recovered.

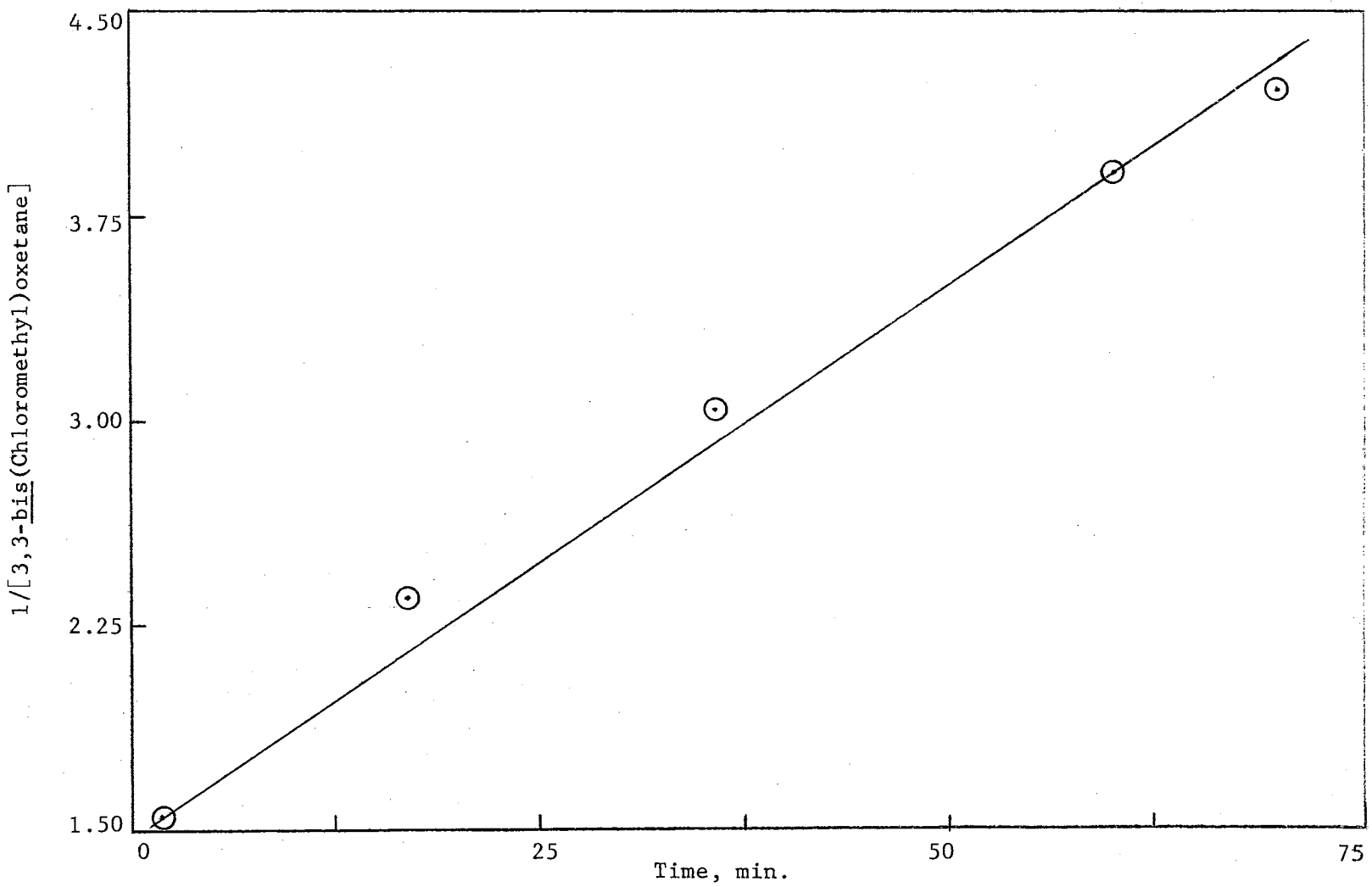


Figure 15. Second-Order Plot for the Acid-Catalyzed Homopolymerization of 3,3-bis(Chloromethyl)oxetane.

DISCUSSION AND CONCLUSIONS

PREPARATIVE AND ANALYTICAL WORK

N-Carboxy Amino Acid Anhydrides and O-Carboxy Hydroxy Acid Anhydrides. Of the various N-carboxy amino acid anhydrides (NCA's) prepared, valine-NCA was found to be most suitable for polymerization because it is readily obtainable in good yield, it has no extra functional groups that must be masked, and most important, its reactivity made it suitable for copolymerization with β-propiolactone. The use of valine-NCA also had some disadvantages. The most serious feature was its failure to yield homopolymers which contained the theoretical percentage of nitrogen. This was very important since the reactivity ratios with propiolactone were determined by using the nitrogen content of the copolymer as a measure of the amount of valine repeating unit in the copolymer. Of the many days spent on this aspect of the problem, most were devoted to analyzing polypeptides by various Kjeldahl procedures. The best value obtained for polyvaline by a Kjeldahl procedure was 13.6 per cent; micro-Dumas gave a maximum of 13.7 per cent; and the theoretical value is 14.1 per cent. Yet the micro-Kjeldahl procedure most used in the present work was found to give good results with simple compounds such as acetanilide and valine.

At least two possible reasons are apparent for the low results of the nitrogen analysis. The first of these is that the polymer was of such low molecular weight that nitrogen-free end groups made a

significant contribution to the composition in the analysis. This is unlikely because of the manner in which NCA's are known to homopolymerize. When primary or secondary amines are used as catalysts, the molecular weight is determined largely by the mole ratio of monomer to initiator. In this investigation the ratio was always large enough that the end groups could not make an appreciable contribution. With tertiary amines and alkoxide catalysts, the molecular weight is even greater than that calculated from the monomer-to-initiator mole ratio (27).

The second possible reason for low values of nitrogen is that organic solvents, or moisture, cling tenaciously to the polymer. Water is definitely retained by some polypeptides (137b). Glycine, its dimer, and trimer show a complete lack of absorption of water vapor. The tetramer and higher polymers, however, do absorb water which is probably hydrogen-bonded to the peptide linkage. The retention of solvents by polymers has been investigated (31a, 86a). One of the investigations noted up to 7 per cent of obstinately trapped solvent in the polymer. This probably accounts for the low results in the present investigation.

Failure to obtain theoretical elemental analyses for polymers is not unusual. The literature contains many examples in which theoretical values could not be obtained (28a, 111a, 142a, 143a, 168a), but the results were still used in copolymer calculations. In particular, results have been only unsatisfactory as reported for polyvaline (98).

Another disadvantage of valine-NCA is that the polypeptide derived from this monomer is insoluble in almost all nondestructive solvents. The literature reports that dichloroacetic acid dissolves polyvaline without extensive degradation (98). Polyvaline produced in the present investigation was indeed soluble in dichloroacetic acid and swelled in

glacial acetic acid-chloroform, but no other solvent was found for the homopolymer.

The failure to obtain a polymer from isatoic anhydride was not entirely unexpected. The rate of propagation of polymerization is dependent upon the basic strength of the terminal amino group which, in this reaction, is very small.

Failure to obtain the OCA of mandelic acid (4-phenyl-1,3-dioxolan-2,5-dione) was probably due to insufficient exposure of the acid to phosgene. The literature (43) specifies a reaction time of several days, whereas in this investigation the reaction was stopped after 5 hours.

β-Lactones. The β-butyrolactone prepared was too impure for kinetic studies. It gave a theoretical neutralization equivalent when heated to 90° in excess base followed, after cooling, by back-titration with standard acid. On the other hand, it also rapidly consumed base at room temperature, probably because of the butyric acid impurity, which could also be smelled. A theoretical neutralization equivalent would be obtained if the lactone was contaminated with butyric acid since the molecular weights of both compounds are very similar. As mentioned earlier, theoretical results could not be obtained with standard $Na_2S_2O_3$ and I_2.

The polyester prepared from β-propiolactone needs no additional comment since it was well described by Gresham, Jansen, and Shaver (90).

Alkene Oxides. Dudek's (50) very recent discovery that relatively concentrated solutions of alkali metal alkoxides can be prepared in tetrahydrofuran seems to offer an excellent opportunity to study the kinetics of polymerization of additional alkene oxides, β-lactones, and

other monomers capable of being polymerized by base. In the present work the lack of a common solvent for one or two cyclic monomers and a strong base (e.g., sodium methoxide or potassium tert-butoxide) was felt keenly.

3,3-bis(Halomethyl)oxetane. The procedure used to prepare 3,3-bis(fluoromethyl)oxetane (BFMO) is probably satisfactory. In view of Campbell's (34) finding that chloride ion is readily displaced from 3,3-bis(chloromethyl)oxetane (BCMO), it seems that the failure to obtain BFMO satisfactorily in the present investigation must be attributed to water in either the potassium fluoride or the ethylene glycol. If this were so, the product would be 3,3-bis(hydroxymethyl)oxetane rather than BFMO. This dihydroxy compound would be soluble in ethylene glycol, as was found, but it would not be a satisfactory monomer for kinetic studies. Under acid-catalyzed conditions it could cross-link and precipitate. Monomers which cross-link were avoided in this investigation, so the product was not isolated.

Alkene Sulfides. While the method developed for determination of propylene sulfide is a satisfactory procedure, it could probably be improved. An occasional sample gives poor results; catalytic amounts of water or other substances may be present which cause the monomer to polymerize rather than quantitatively react with the ring-opening reagent.

This seems the place to include some information on a possible method for determining tetrahydrofuran in solution. The same procedure as used to determine propylene sulfide gave 88 per cent of the theoretical value for a solution of tetrahydrofuran in CH_2Cl_2. The tetrahydrofuran was reagent material, but it was not dried before use. Because of the pressure of other work, the procedure was not developed further.

Copolymers. Copolymers can be prepared by reacting excess β-propiolactone with the N-carboxy amino acid anhydrides (NCA's). The properties of the copolymers will not be reviewed, but it is apparent that the molecular weights are too low to permit the formation of fibers. These copolymers are probably of a random pattern. There is no evidence of the regular alternation of repeating units usually found in vinyl copolymers produced by radical catalysts.

The copolymers of valine-NCA and β-propiolactone have never been prepared, but a few polymers made with α-amino acid and α-hydroxy acid repeating units have been described (158a). These copolymers are known as depsipeptides, and are made by a stepwise procedure and not from NCA's.

The NCA of α-aminoisobutyric acid is less reactive than valine-NCA (175). Therefore it should be a satisfactory monomer for future studies of depsipeptides. However, the polypeptide would still be difficult to study since it would likely be insoluble in most solvents.

The failure of the attempted copolymerization of propylene sulfide and propiolactone was surprising. Propylene sulfide, which is normally quite reactive, did not even homopolymerize, at least not to solid polymer. Similar results have been reported for propylene oxide and β-propiolactone, the epoxide remaining unchanged (109).

As previously mentioned, only by using an excess of a very reactive beta-lactone with a relatively unreactive N-carboxy amino acid anhydride can copolymers be prepared. Dermer (47) found essentially the same to be true of alkene sulfides and alkene oxides; that is, the least reactive monomer, the oxide in this case, had to be present in large excess before any of its repeating unit could definitely be

detected in the copolymer.

If cyclic monomers of different families must be of about the same reactivity before they will copolymerize, as is indicated by the previous examples, it seems evident that the copolymerization of cyclic monomers is more difficult than radical copolymerization. In radical copolymerization it is not necessary to search for monomers of about the same reactivity. As a matter of fact, monomers which are very difficult to homopolymerize have been observed to copolymerize in radical processes (3).

KINETICS OF COPOLYMERIZATION

The monomer reactivity ratios of the classical copolymer composition equation are defined as the ratios of the rate constants for a given terminal unit adding to its own monomer to that for addition to the other monomer. Therefore, the negative monomer reactivity ratio determined for β-propiolactone in the lactone-valine-NCA copolymerization has no physical meaning. The numerical value is somewhat doubtful as to magnitude since theoretical percentage of nitrogen could not be obtained for polyvaline. Negative ratios have been obtained before (47, 160a). Such values are sometimes considered to be zero (68, 160a). If this is done in the present investigation, the interpretation is that whenever the reactive end of the growing copolymer is derived from propiolactone it adds only valine-NCA. Qualitatively all that can be said of the $r_1 = 11$ value is that a terminal amino group of valine-NCA repeating unit has a considerable tendency to add another NCA rather than β-propiolactone.

Perhaps it would be better to report a single relative reactivity

ratio as Dermer (47) and Bailey and France (6) have done. This ratio in the present work, as in Dermer's investigation, was determined by plotting the log of the per cent of unreacted monomers as ordinate and abscissa. The slope of the line through the points is the relative reactivity ratio. This is the alpha value of the integrated form of Wall's (173) copolymer equation. The procedure used to calculate these values is known as the Lee homocompetitive method (124). The value for valine-NCA and β-propiolactone is 117; that is, valine-NCA is 117 times as reactive as the lactone in this situation. Dermer's alpha values are 215, 215, 5.4, and 1 respectively for ethylene sulfide, propylene sulfide, N-ethylethylenimine, and ethylene oxide. Bailey and France reported the following values: ethylene oxide/styrene oxide, 1.0; ethylene oxide/propylene oxide, 1.3; ethylene oxide/allyl glycidyl ether, 1.5; ethylene oxide/butadiene monoxide, 3. Ethylene oxide can be assigned a relative value of one in the series of Bailey and France. Since ethylene oxide has a value of one in Dermer's work, results of the investigations can be combined into a series of relative reactivities. This series in decreasing order of relative reactivity is: ethylene sulfide = propylene sulfide >> N-ethylethylenimine > ethylene oxide = styrene oxide > propylene oxide > allyl glycidyl ether > butadiene monoxide. Also since propylene sulfide failed to polymerize in the presence of β-propiolactone and catalyst, valine-NCA and the beta-lactone, in that order, could be placed at the head of the series. Since different bases were used as catalysts in these copolymerizations, the order of reactivity may not have much significance, although Bailey and France found their order to be independent of the nature of the basic catalyst.

The alpha values obtained by Katchalski and Shalitin (162) were not determined by competitive experiments, but are actually the ratios of the rate constants of homopolymerization.

In the present investigation no alpha values were determined by this method because no comparable pairs of reaction rate constants for homopolymerization could be obtained. The kinetics of the reactions were mostly complex. Only with β-propiolactone and epichlorohydrin as monomers were simple pseudo first-order kinetics observed, and unfortunately the first of these reactions was base-catalyzed and the second acid-catalyzed.

It was still possible, however, to test the Katchalski-Shalitin (162) observation that the rate of copolymerization is sometimes equal to the sum of the rates of homopolymerization. N-(2-Hydroxyethyl)aziridine (NHEA) and N-(2-hydroxy-n-propyl)aziridine (NHPA) polymerize in this manner as shown by Figure 14, but Figure 10 shows that propylene oxide and epichlorohydrin do not. The tendency of alkene oxides to form dimers in the presence of acid may account for the lack of additivity in their rates of polymerization.

The homopolymerizations of both NHEA and NHPA are more complex than pseudo first- or second-order. These experiments were repeated and essentially the same results were obtained. Since the reaction rate decreases rapidly as the polymer is formed, apparently the catalyst is progressively consumed or otherwise inactivated as the reaction proceeds. If the polymer is more basic than the monomer, it may effectively reduce the concentration, or rather the activity, of hydrogen ion available to the monomer. However, Barb (13a) showed that the presence of extraneous amine does not greatly decrease the rate of polymerization of

ethylenimine and concluded that the catalyst was actually destroyed during reaction. Hence, this is also likely in the homopolymerization of NHEA and NHPA, although no experiments were performed in the presence of added alkylamines. In the uncatalyzed reaction in H_2O at 100° the homopolymerizations of NHEA and NHPA are pseudo first order, probably because of the constant proton supply (140a).

The BF_3-initiated homopolymerization of ethylene oxide has been well studied (124a, 180b). The reaction was shown to be 0.67 order in monomer concentration. This reaction was found to be very complex. Whether the initial reactant is monomer or a mixture of monomer and high molecular weight polymer, the molecular weight of the product becomes constant at approximately 700, and dioxane is produced. The dioxane arises by a reaction between polymer and oxonium ions.

Since the BF_3-initiated homopolymerization of ethylene oxide is so complex, and since data of this kind were not obtained for propylene oxide, no conclusions can be made about the homopolymerization of the latter monomer. However, it was observed that after an initial rapid reaction the kinetics do seem to approach first order. This has also been observed with a ferric chloride-propylene oxide-complex catalyst (81). In this investigation the change in order was attributed to a change in the nature of the iron-containing catalyst.

The BF_3-initiated homopolymerization of 3,3-bis(chloromethyl)oxetane was found to be second order in monomer concentration. Rose (156) studied the homopolymerization of 3,3-dimethyloxetane. The reaction was found to be first order in monomer with BF_3 catalyst. If water was used as cocatalyst, however, the reaction became second order in monomer concentration.

The Katchalski-Shalitin (162) observation could not be tested with 3,3-bis(chloromethyl)oxetane and 3,3-bis(iodomethyl)oxetane because the homopolymerization of the latter monomer rapidly became heterogeneous.

Much more work remains to be done in the kinetics of ring-scission copolymerization. The Katchalski-Shalitin theory (162) should be tested more completely. Alpha values should be obtained and the copolymer composition equation tested. Alkoxide-initiated homopolymerizations in tetrahydrofuran are particularly recommended for study.

BIBLIOGRAPHY

1. Adelson, D.E., Perry, G.O., and Pritzker, G.G. (to Shell Development Co.), U.S. 2,628,941 (1953) via C.A. 47, 4600.

2. Alfrey, Jr., T., and Goldfinger, G., J. Chem. Phys., 12, 205 (1944).

3. Alfrey, Jr., T., Bohrer, J.J., and Mark, H., Copolymerization, Interscience Publishers, Inc., New York, 1952.

4. Astle, M.J. in Hamor, W.A. (ed.), A.C.S. Monograph 150, Industrial Organic Nitrogen Compounds, Reinhold Publishing Corp., New York, 1961, Chapter 3.

5. Averell, P.R., in Kline, G.O. (ed.), High Polymers, Vol XII, Interscience Publishers, Inc., New York, 1959, p. 71-72.

6. Bailey, Jr., F.E., and France, H.J., J. Polymer Sci., 45, 243 (1960).

7. Bailey, J.L., J. Chem. Soc., 3461 (1950).

8. Ballard, D.G.H., and Bamford, C.H., Proc. Roy. Soc. (London), A223, 495 (1954).

9. Ballard, D.G.H., and Bamford, C.H., Proc. Roy. Soc. (London), A236, 384 (1956).

10. Ballard, D.G.H., and Bamford, C.H., J. Chem. Soc., 381 (1956).

11. Ballard, D.G.H., and Bamford, C.H., J. Chem. Soc., 1039 (1959).

12. Ballard, D.G.H., Bamford, C.H., and Elliott, A., Makromol. Chem., 35, 222 (1960).

13. Bamford, C.H., Elliott, A., and Hanby, W.E., Synthetic Polypeptides, Academic Press, Inc., New York, 1956.

13a. Barb, W.G., J. Chem. Soc., 2546 (1955).

13b. Barb, W.G., J. Chem. Soc., 2577 (1955).

14. Bell, E.V., Bennett, G.M., and Hock, L.A., J. Chem. Soc., 1803 (1927).

15. Ben-Ishai, D., and Berger, A., J. Org. Chem., 17, 1564 (1952).

16. Ben-Ishai, D., and Katchalski, E., J. Am. Chem. Soc., 74, 3688 (1952).

17. Berger, A., and Katchalski, E., J. Am. Chem. Soc., 73, 4084 (1951).

18. Bergmann, M., and Zervas, L., Ber., 65, 1192 (1932).

19. Bergmann, M., Zervas, L., and Ross, W.F., J. Biol. Chem., 111, 245 (1935).

20. Berlow, E., Barth, R.H., and Snow, J.E., in Hamor, W.A. (ed.), A.C.S. Monograph 136, The Pentaerythritols, Reinhold Publishing Corp., New York, 1958, Chapter 10.

21. Berthelot, M., Ann. chim. et phys. (3) 41, 299 (1854) via A.C.S. Monograph 114, Glycols, Reinhold Publishing Corp., New York, 1952, Chapter 5.

22. Bestian, H., in Müller, E. (ed.), Methoden der organischen Chemie, Vol. 11, part 2, G. Thieme, Stuttgart, 1958, p. 227-265.

23. Bestian, H., and Karrenbauer, K. (Farbwerke Hoechst, A.G.), Ger. 914, 325 (1954) via C.A. 52, 11471.

24. Bestian, H., and Karrenbauer, K. (Farbwerke Hoechst, A.G.), Ger. 915, 743 (1954) via C.A. 52, 11471.

25. Bickel, C.L., J. Am. Chem. Soc., 68, 941 (1946).

26. Billmeyer, Jr., F.W., Textbook of Polymer Chemistry, Interscience Publishers, Inc., New York, 1957.

27. Blout, E.R., and Karlson, R.H., J. Am. Chem. Soc., 78, 941 (1956).

28. Bordwell, F.G., and Andersen, H.M., J. Am. Chem. Soc., 75, 4959 (1953).

28a. Breslow, D.S., and Kutner, A., J. Polymer Sci., 27, 305 (1958).

29. Brown, C.J., Coleman, D., and Farthing, A.C., Nature, 163, 834 (1949).

30. Buist, G.J., and Lucas, H.J., J. Am. Chem. Soc., 79, 6157 (1957).

31. Calingaert, G., Bull. soc. chim. Belg., 31, 109 (1922) via C.A. 16, 3870.

31a. Cameron, G.G., Grant, D.H., Grassie, N., Lamb, J.E., and McNeill, I.C., J. Polymer Sci., 36, 173 (1959).

32. Campbell, K.N., Campbell, B.K., McKenna, J.F., and Chaput, E.P., J. Org. Chem., 8, 103 (1943).

33. Campbell, T.W. (to E.I. du Pont de Nemours and Co.), U.S. 2,831,825 (1958) via C.A. 52, 13316.

34. Campbell, T.W., J. Org. Chem., 22, 1029 (1957).

35. Carothers, W.H., J. Am. Chem. Soc., 51, 2548 (1929).

36. Closs, G.L., and Brois, S.J., J. Am. Chem. Soc., 82, 6068 (1960).

37. Coleman, D., J. Chem. Soc., 2294 (1951).

38. Coltoff, W. (to Shell Development Co.), U.S. 2,183,860 (1940) via C.A. 34, 2395.

39. Coltoff, W., and Langedijk, S.L. (to Shell Development Co.), U.S. 2,185,660 (1940) via C.A. 34, 2865.

40. Curme, Jr., G.O. (ed.), and Johnston, F. (associate ed.), A.C.S. Monograph 114, Glycols, Reinhold Publishing Corp., New York, 1952, Chapter 7.

41. Curtius, T., and Sieber, W., Ber., 54, 1430 (1921).

42. Curtius, T., and Sieber, W., Ber., 55, 1543 (1922).

43. Davies, W.H., and Imperial Chemical Industries, Ltd., Brit. 650,003 (1951).

44. Davies, W., and Savige, W.E., J. Chem. Soc., 317 (1950).

45. Delépine, M., Bull. soc. chim. France, 27, 740 (1920) via C.A. 15, 53.

46. Delépine, M., Compt. rend., 171, 36 (1920) via C.A. 14, 3226.

47. Dermer, O.C., WADC Technical Report 55-447, Copolymers of Olefin Sulfides (1956).

48. Dostal, H., Monatsh., 69, 424 (1936) via Mayo, F.R., and Walling, C., Chem. Rev., 46, 191 (1950).

49. Doty, P., and Lundberg, R.D., J. Am. Chem. Soc., 78, 4810 (1956).

50. Dudek, J.T., Diss. Absts., 22, 1407 (1961); Ph.D. Dissertation, University of Akron, 1961.

51. Eastham, A.M., Fortschr. Hochpolymer-Forsch., 2, 18 (1960).

52. Eastham, A.M., Fortschr. Hochpolymer-Forsch., 2, 37 (1960).

53. Eastman Chemical Products, Inc., Technical Data Report # X-129 (1961).

54. Einhorn, A., Ber., 16, 2208 (1883).

55. Eirich, F., Katchalski, E., Reisman, J., and Spitnik, P., Unpublished results via Katchalski, E., Advances in Protein Chemistry, VI, Academic Press, Inc., New York, N.Y., 1951, p. 166.

56. Elderfield, R.C., and Hageman, H.A., J. Org. Chem., 14, 607 (1949).

57. Eliel, E.L., Stereochemistry of Carbon Compounds, McGraw-Hill Book Co., Inc., New York, 1962, p. 446-453.

58. Erlenmeyer, E., Ber., 13, 303 (1880).

59. Etienne, Y., Ind. Plastiques Mod. (Paris), 9, 37 (1957) via Sorenson, W.R., and Campbell, T.W., Preparative Methods of Polymer Chemistry, Interscience Publishers, Inc., New York, 1961, p. 253.

60. Ettlinger, M.G., J. Am. Chem. Soc., 72, 4792 (1950).

61. Farthing, A.C., J. Chem. Soc., 3213 (1950).

62. Farthing. A.C., J. Chem. Soc., 3648 (1955).

63. Farthing, A.C., Chem. and Ind. (London), 594 (1957).

64. Farthing, A.C., and Reynolds, R.J.W., Nature, 165, 647 (1950).

65. Fedor, W.S., Chem. Eng. News, 39, No. 12, 125 (1961).

66. Fessler, J.J., and Ogston, A.G., Trans. Faraday Soc., 47, 667 (1951).

67. Fieser, L.F., Experiments in Organic Chemistry, 3rd ed., D.C. Heath and Co., Boston, 1957, p. 287.

68. Fineman, M., and Ross, S.D., J. Polymer Sci., 5, 259 (1950).

69. Flory, P.H., Principles of Polymer Chemistry, Cornell University Press, Ithaca, New York, 1953.

70. Frankel, M., and Berger, A., J. Org. Chem., 16, 1513 (1951).

71. Frankel, M., and Halmann, M., J. Chem. Soc., 2735 (1952).

72. Frankel, M., Cordova, S., and Breuer, M., J. Chem. Soc., 1991 (1953).

73. Frear, D.E.H., and Seiferle, E.J., J. Econ. Entomol., 40, 736 (1947).

73a. Fritz, T.S., and Lisick, N.M., Anal. Chem., 23, 589 (1951).

74. Fuchs, F., Ber., 55, 2943 (1922).

75. Furukawa, K., and Oda, R., Bull. Inst. Chem. Research, Kyoto Univ., 30, 50 (1952) via C.A. 47, 3611.

76. Furukawa, K., Nomura, M., and Oda, R., Bull. Inst. Chem. Research, Kyoto Univ., 28, 74 (1952) via C.A. 46, 11105.

77. Furukawa, K., Nomura, M., and Oda, R., J. Chem. Soc. Japan, Ind. Chem. Section, 56, 184 (1953) via C.A. 49, 4581.

78. Gabriel, S., Ber., 21, 1049 (1888).

79. Gabriel, S., and Stelzner, R., Ber., 28, 2929 (1895).

80. Gaylord, N.G., and Mark, H.F. in Polymer Reviews, Vol. 2, Linear and Stereoregular Addition Polymers, Interscience Publishers, Inc., New York, N. Y., 1959, Chapter X.

81. Gee, G., Higginson, W.C.E., and Jackson, J.B., Polymer, 3, 231 (1962).

82. Gee, G., Higginson, W.C.E., and Merrall, G., J. Chem. Soc., 1345 (1959).

83. Gilman, H., Beel, J.A., Brannen, C.G., Bullock, M.W., Dunn, G.E., and Miller, L.S., J. Am. Chem. Soc., 71, 1499 (1949).

84. Go, Y., and Tani, H., Bull. Chem. Soc. Japan, 14, 510 (1939).

85. Goldstein, R.F., The Petroleum Chemical Industry, 2nd ed., John Wiley and Sons, Inc., New York, 1958, Chapters 9,10,19.

86. Goodman, M., Abstracts of Papers, 15U, Division of Polymer Chemistry, 140th meeting, ACS, Chicago, Ill., Sept., 1961.

86a. Grassie, N., J. Polymer Sci., 6, 643 (1951).

87. Green, M., and Stahmann, M.A., J. Biol. Chem., 197, 771 (1952).

88. Gresham, T.L., and Jansen, J.E. (to B.F. Goodrich Co.), U.S. 2,449,990 (1948) via C.A. 43, 1053.

89. Gresham, T.L., and Jansen, J.E. (to B.F. Goodrich Co.), U.S. 2,526,554 (1950) via C.A. 45, 2500.

90. Gresham, T.L., Jansen, J.E., and Shaver, F.W., J. Am. Chem. Soc., 70, 998 (1948).

91. Gresham, T.L., Jansen, J.E., and Shaver, F.W., J. Am. Chem. Soc., 70, 1003 (1948).

92. Gresham, T.L., Jansen, J.E., Shaver, F.W., and Gregory, T.J., J. Am. Chem. Soc., 70, 999 (1948).

93. Gresham, T.L., Jansen, J.E., Shaver, F.W., Bankert, R.A., and Fiedorek, F.T., J. Am. Chem. Soc., 73, 3168 (1951).

94. Gresham, T.L., Shaver, F.W., Gregory, T.J., and Beears, W.L., J. Am. Chem. Soc., 1004 (1948).

95. Hagemeyer, Jr., H.J., Ind. Eng. Chem., 41, 765 (1949).

96. Hall, Jr., H.K., and Schneider, A.K., J. Am. Chem. Soc., 80, 6409 (1958); Hall, Jr., H.K., J. Am. Chem. Soc., 80, 6404 (1958).

97. Hanby, W.E., Waley, S.G., and Watson, J., Nature, 161, 132 (1948).

98. Hanby, W.E., Waley, S.G., and Watson, J., J. Chem. Soc., 3009 (1950).

99. Hanby, W.E., Waley, S.G., and Watson, J., J. Chem. Soc., 3239 (1950).

100. Harrington, C.R., and Mead, T.H., J. Biol. Chem., 130, 81 (1935).

101. Hasek, R.H., Clark, R.D., Elam, E.U., and Martin, J.C., J. Org. Chem., 27, 60 (1962).

102. Heine, H.W., Kapur, B.L., and Mitch, C.S., J. Am. Chem. Soc., 76, 1173 (1954).

103. Holden, R.F., in Curme, Jr., G.O. (ed.), A.C.S. Monograph 114, Glycols, Reinhold Publishing Corp., New York, 1952, Chapter 11, 13.

104. Holmberg. B., Svensk Kem. Tidskrift, 30, 190-205,215-222 via Zaugg, H.E., Org. Reactions, VIII, John Wiley and Sons, Inc., New York, 1954, Chapter 7.

105. Hurd, C.D., and Buess, C.M., J. Am. Chem. Soc., 73, 2409 (1951).

106. Idelson, M., and Blout, E.R., J. Am. Chem. Soc., 79, 3948 (1957).

107. Idelson, M., and Blout, E.R., J. Am. Chem. Soc., 80, 2387 (1958).

108. I.G. Farbenind., A.-G., Fr. 803,509 (1936) via C.A. 31, 2736.

109. Inoue, S., Tomoi, Y., Tsuruta, T., and Furukawa, J., Makromol. Chem., 48, 229 (1961).

110. Ishida, S., Bull. Chem. Soc., Japan, 33, 731 (1960).

111. Iwakura, Y., Nagakubo, K., Aoki, J., and Yamada, A., Nippon Kagaku Zasshi, 75, 315 (1954) via C.A 51, 11246.

111a. Iwakura, Y., Tamikodo, T., Yamaguchi, M., and Takei, K., J. Polymer Sci., 39, 203 (1959).

112. Jansen, J.E., (to B.F. Goodrich Co.), U.S. 2,623,070 (1952) via C.A. 47, 3039.

113. Jansen, J.E., and Beears, W.L. (to B.F. Goodrich Co.), U.S. 2,568,635 (1951) via C.A. 46, 3557.

114. Johansson, H., Lunds Universitets Arsskrift, N.F., Avd. 2, 12, No. 8; Kungl. Fysiografiska Sällskapets Handlingar, N.F., 27, No. 8 via C.A. 11, 2576.

115. Jones, G.D., J. Org. Chem., 9, 484 (1944).

116. Jones, G.D., Langsjoen, A., Neumann, M.M.C., and Zomlefer, J., J. Org. Chem., 9, 125 (1944).

117. Jungnickel, J.L., Peters, E.D., Polgar, A., and Weiss, F.T., Organic Analysis, Vol.I, Interscience Publishers, Inc., New York, 1953, p. 127-154.

118. Katchalski, E., Adv. in Protein Chem., VI., Academic Press, Inc., New York, N. Y., 1951, p. 123-185.

119. Katchalski, E., and Sela, M., Adv. in Protein Chem., XIII, Academic Press, Inc., New York, N. Y., 1958, p. 224-475.

120. Katchalski, E., Grossfeld, I., and Frankel, M., J. Am. Chem. Soc., 70, 2094 (1948).

121. Kodak-Pathé (by Etienne, Y. and Fischer, N.), Fr. 1,231,163 (1960) via C.A. 55, 19330.

122. Kohler, E.P., and Bickel, C.L., J. Am. Chem. Soc., 63, 1531 (1941).

123. Küchler, L., Polymerisationskinetik, Springer-Verlag, Berlin, p. 4.

123a. Kuntz, I., J. Polymer Sci., 54, 569 (1961).

124. Lasselle, P.A., and Sundet, S.A., J. Am. Chem. Soc., 63, 2374 (1941).

124a. Latremouille, G.A., Merrall, G.T., and Eastham A.M., J. Am. Chem. Soc., 82, 120 (1960).

124b. Lee, T.S., in Technique of Organic Chemistry, Vol. VIII, Investigation of Rates and Mechanisms of Reactions, Interscience Publishers, Inc., New York, 1953, p. 100.

125. Leuchs, H., Ber., 39, 857 (1906).

126. Leuchs, H., and Geiger, W., Ber., 41, 1721 (1908).

127. Levy, A.L., Nature, 165, 152 (1950).

128. Long, F.A., and Purchase, M., J. Am. Chem. Soc., 72, 3267 (1950).

129. Lundberg, R.D., and Doty, P., J. Am. Chem. Soc., 79, 3961 (1957).

130. Machell, G., Ind. Chemist, 36, 13 (1960).

131. Marckwald, W., Ber., 33, 764 (1900).

132. Marrian, J., Chem. Rev., 43, 149 (1948).

133. Marvel, C.S., and Schertz, G.L., J. Am. Chem. Soc., 65, 2054 (1943).

134. Marvel, C.S., and Weil, E.D., J. Am. Chem. Soc., 76, 68 (1954).

135. Marvel, C.S., Jones, G.D., Mastin, T.W., and Schertz, G.L., J. Am. Chem. Soc., 64, 2356 (1942).

136. Mayo, F.R., and Lewis, F.M., J. Am. Chem. Soc., 66, 1594 (1944).

137. Mayo, F.R., and Walling, C., Chem. Rev., 46, 191 (1950).

137a. Meerwein, H., Delfs, D., and Morschel, H., Angew. Chem., 72, 927 (1960).

137b. Mellon, E.F., Korn, A.H., and Hoover, S.R., J. Am. Chem. Soc., 70, 3040 (1948).

137c. Merrall, G.T., Latremouille, G.A., and Eastham, A.M., Can. J. Chem., 38, 1967 (1960).

138. Meyer, K.H., and Go, Y., Helv. Chim. Acta., 17, 1488 (1934).

139. Meyer, V., Ber., 19, 3262, (1886).

140. Miller, L., and Houghton, J.A., J. Biol. Chem., 159, 373 (1945).

140a. Miller, G.R., Private Communication.

141. Minoura, Y., Takebayashi, M., and Price, C.C., J. Am. Chem. Soc., 81, 4689 (1959).

142. Mitchell, J.C., Woodward, A.E., and Doty, P., J. Am. Chem. Soc., 79, 3955 (1957).

142a. Moos, G.E., Budelman, H., and Chen, P.F., J. Polymer Sci., 33, 273 (1958).

143. Murback, W.J., and Adicoff, A., Ind. Eng. Chem., 52, 772 (1960).

143a. Nozaki, K., J. Polymer Sci., 1, 455 (1946).

144. N.V. de Bataafsche Petroleum Maatschappij, Fr. 819,995 (1937) via C.A. 32, 3064.

145. N.V. de Bataafsche Petroleum Maatschappij, Brit. 508,932 (1939) via C.A. 34, 2863; Fr. 850,242 (1939) via C.A. 36, 1614.

146. Olin, J.F., and Dains, F.B., J. Am. Chem. Soc., 52, 3322 (1930).

147. Olson, A.R., and Hyde, J.L., J. Am. Chem. Soc., 63, 2459 (1941).

148. Olson, A.R., and Miller, R.J., J. Am. Chem. Soc., 60, 2687 (1938).

149. Oser, B., Ann. Suppl., 1, 253 (1861) via Holden, R.F., in Curme, Jr., G.O. (ed.), A.C.S. Monograph 114, Glycols, Reinhold Publishing Corp., New York, 1952, Chapter 11.

150. Patchornik, A., Berger, A., and Katchalski, E., J. Am. Chem. Soc., 79, 5227 (1957).

151. Perry, S., and Hibbert, H., J. Am. Chem. Soc., 62, 2599 (1940).

152. Price, C.C., and Kirk, P.F., J. Am. Chem. Soc., 75, 2396 (1953).

153. Price, C.C., Takebayashi, M., and Minoura, Y., Abstracts of Papers, 10P, Division of Paint, Plastics, and Printing Ink Chemistry, 135th Meeting, ACS, Boston, Mass., April 1959.

153a. Priest, W.J., in Technique of Organic Chemistry, Vol. VIII, Investigations of Rates and Mechanisms of Reactions, Interscience Publishers, Inc., New York, 1953, p. 456.

154. Ray, F.E., and Levine, I., J. Org. Chem., 2, 271 (1937).

155. Reid, E.E., Organic Chemistry of Bivalent Sulfur, Vol. III, Chemical Publishing Co., Inc., New York, N. Y., 1960, p. 13-19,89.

156. Rose, J.B., J. Chem. Soc., 546 (1956).

157. Saegusa, T., Imai, H., Hirai, S., and Furukawa, J., Makromol. Chem., 53, 203 (1962).

158. Sandiford, D.J.H., Chem. and Ind. (London), 594 (1957).

158a. Schemjakin, M.M., Angew. Chem., 71, 741 (1959).

158b. Schoberl, A., Makromol. Chem., 37, 64 (1960).

159. Schönberg. A., in Müller, E. (ed.), Methoden der organischen Chemie, Vol. 9., G. Thieme, Stuttgart, 1955, p. 153.

160. Schultze, H.C., in Curme, Jr., G.O. (ed.), A.C.S. Monograph 114, Glycols, Reinhold Publishing Corp., New York, 1952, Chapter 5.

160a. Schwan, T.C., and Price, C.C., Proc. Indiana Acad. Sci., 63, 103 (1953); C.A. 49, 5941.

160b. Searles, Jr., S., and Lutz, E.F., J. Am. Chem. Soc., 80, 3168 (1958).

161. Sela, M., and Berger, A., J. Am. Chem. Soc., 77, 1893 (1955).

162. Shalitin, Y., and Katchalski, E., J. Am. Chem. Soc., 82, 1630 (1960).

163. Sigmund, F., and Wessely, F., Z. physiol. Chem., 157, 91 (1926) via C.A. 21, 377.

164. Sixt, J. (to Wacker-Chemie, G.m.b.H.), U.S. 2,763,664 (1956); C.A. 51, 5115.

165. Smith, P.A.S., Org. Reactions, Vol. III, John Wiley and Sons, Inc., New York, 1946, p. 337.

166. Staudinger, H., and Schweitzer, O., Ber., 62, 2395 (1929).

167. Steinbach, O.F., and King, C.V., Experiments in Physical Chemistry, American Book Co., New York, 1950, p. 13-15.

168. Tarbell, D.S., and Harnish, D.P., Chem. Rev., 49, 18 (1951).

168a. Thompson, B.R., J. Polymer Sci., 19, 373 (1956).

169. van Tamelen, E.E., J. Am. Chem. Soc., 73, 3444 (1951).

170. Wagner, E.C., and Fegley, M.F., in Horning, E.C. (ed.), Org. Synthesis, Coll. Vol. III, John Wiley and Sons, Inc., New York, p. 488.

171. Waley, S.G., and Watson, J., Proc. Roy. Soc. (London), A199, 499 (1949).

172. Waley, S.G., and Watson, J., Rec. trav. chim., 69, 27 (1950).

173. Wall, F.T., J. Am. Chem. Soc., 63, 1862 (1941).

174. Wall, F.T., J. Am. Chem. Soc., 66, 2050 (1944).

175. Weingarten, H., J. Am. Chem. Soc., 80, 352 (1958).

176. Wenker, H., J. Am. Chem. Soc., 57, 2328 (1935).

177. Wessely, F., Z. physiol. Chem., 146, 72 (1925) via C.A. 19, 3083.

178. Wessely, F., and Sigmund, F., Z. physiol. Chem., 159, 102 (1926) via C.A. 21, 389.

179. Wolfheim, F., Ber., 47, 1450 (1914).

180. Woodward, R.B., and Schramm, C.H., J. Am. Chem. Soc., 69, 1551 (1947).

180a. Worsfold, D.J., and Eastham, A.M., J. Am. Chem. Soc., 79, 897 (1957).

180b. Worsfold, D.J., and Eastham, A.M., J. Am. Chem. Soc., 79, 900 (1957).

181. Wurtz, A., Ann., 110, 125 (1859); Ann. chim. et phys. (3) 55, 433 (1859) via Schultze, H.C., in Curme, Jr., G.O. (ed.), A.C.S. Monograph 114, Glycols, Reinhold Publishing Corp., New York, 1952, Chapter 5.

182. Wurtz, A., Ber., 10, 90 (1877) Bull. soc. chim. France (2) 29, 530 (1878) via Curme, Jr., G.O. (ed.), A.C.S. Monograph 114, Glycols, Reinhold Publishing Corp., New York, 1952, Chapter 7.

183. Zaugg, H.E., in Org. Reactions, Vol. VIII, John Wiley and Sons, Inc., New York, 1954, Chapter 7.

A P P E N D I C E S

APPENDIX I

The Fineman-Ross form of the copolymer composition equation is presented in the text. The calculations are presented in Table I.

TABLE I

CALCULATION FOR THE FINEMAN-ROSS TREATMENT OF DL-VALINE-NCA AND β-PROPIOLACTONE

f_1	f_1^2	$(1-f_1)$	$(1-f_1)^2$	F_1	$1-2F_1$	F_1-1
0.053	0.0028	0.947	0.897	0.607	-0.214	-0.393
0.123	0.0151	0.877	0.769	0.848	-0.696	-0.152
0.200	0.0400	0.800	0.640	0.896	-0.792	-0.104
0.351	0.1232	0.640	0.421	0.931	-0.862	-0.069
0.639	0.4083	0.361	0.130	0.944	-0.888	-0.056
0.800	0.6400	0.200	0.040	0.981	-0.962	-0.019

$f_1(1-2F_1)$	$(1-f_1)F_1$	$f_1^2(F_1-1)$
-0.0113	0.5748	-0.0011
-0.0856	0.7437	-0.0023
-0.1584	0.7168	-0.0042
-0.3025	0.6042	-0.0085
-0.5674	0.3408	-0.0229
-0.7696	0.1962	-0.0122

$(1-f_1)^2F_1$	$\frac{f_1(1-2F_1)}{(1-f_1)F_1}$	$\frac{f_1^2(F_1-1)}{(1-f_1)^2F_1}$
0.5445	-0.0197	-0.0020
0.6521	-0.1151	-0.0035
0.5734	-0.2210	-0.0073
0.3920	-0.5007	-0.0217
0.1227	-1.6649	-0.1866
0.0392	-3.9225	-0.3112

APPENDIX II

The values of slope and intercept for the six linear equations were determined by the method of least squares. The calculations are presented in Table II.

TABLE II

LEAST SQUARES TREATMENT OF FINEMAN-ROSS DATA FOR DL-VALINE-NCA AND β-PROPIOLACTONE

y	x	x^2	xy
0.0197	0.0020	0.00000400	0.00003940
0.1151	0.0035	0.00001225	0.00040285
0.2210	0.0073	0.00005329	0.00161330
0.5007	0.0217	0.00047089	0.01086519
1.6649	0.1866	0.03481956	0.31067034
3.9225	0.3112	0.09684544	1.22068200
$\Sigma y = 6.4439$	$\Sigma x = 0.5323$	$\Sigma x^2 = 0.1322$	$\Sigma xy = 1.5443$

Intercept (b) is given by:

$$b = \frac{\Sigma X \cdot \Sigma(Xy) - \Sigma X^2 \cdot \Sigma y}{[\Sigma(X)]^2 - n\Sigma(X^2)} \quad \text{where } n = 6$$

$b = 0.16$ or $r_{\text{propiolactone}} = -0.16$

Slope (m) is given by:

$$m = \frac{\Sigma(X) \cdot \Sigma(y) - n\Sigma(Xy)}{[\Sigma(X)]^2 - n\Sigma(X^2)}$$

$m = 11$ or $r_{\text{valine-NCA}} = 11$

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