I. SYNTHESIS AND POLYMERIZATION OF NORTRICYCLENE DERIVATIVES

II. 1:1 ALTERNATING COPOLYMERS OF BICYCLOBUTANES

by

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ABSTRACT

1-Acetylnortricyclene and 1-nortricyclenecarbonitrile were synthesized. Several attempts were made to homopolymerize and copolymerize 1-acetylnortricyclene. Attempts to initiate homopolymerization with either sodium or di-t-butyl peroxide failed, even at 200°. Free radical copolymerization of 1-acetylnortricyclene and styrene with azobisisobutyronitrile as initiator and anionic copolymerization with sodium-naphthalene as initiator were unsuccessful. In both cases only polystyrene was obtained. Copolymerization of 1-acetylnortricyclene and vinyl chloride with potassium persulfate as initiator was likewise unsuccessful, resulting only in poly(vinyl chloride).

1:1 Copolymers of 1-bicyclobutanecarbonitrile and styrene, and of methyl 1-bicyclobutanecarboxylate and styrene, were prepared by complexing the electron-poor monomer with zinc chloride. In the case of 1-bicyclobutanecarbonitrile and styrene, the polymer formed was shown to be alternating. Homopolymers of

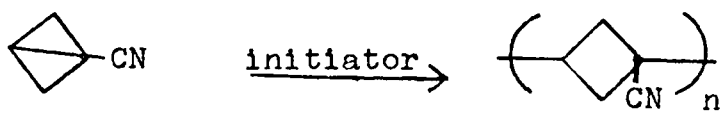
1-bicyclobutanecarbonitrile and of methyl 1-bicyclobutanecarboxylate were also prepared with zinc chloride as initiator. The mechanisms of these polymerizations were briefly explored.

PART I

SYNTHESIS AND POLYMERIZATION OF NORTRICYCLENE DERIVATIVES

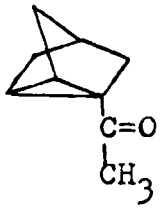
INTRODUCTION

In the past there have been several attempts to polymerize compounds containing cyclopropane rings via ring-opening. Most momocyclic cyclopropanes polymerize poorly or not at all. More success has been had with bicyclic cyclopropane-containing compounds. Pinazzi et al. (1968) have described low polymers from bicyclo[n.1.0] alkanes and Wiberg (1965) and Wiberg et al. (1965) have shown that methyl and ethyl 1-bicyclobutanecarboxylates polymerize when left at room temperature. More recently, Hall et al. (1971a,-b) and Swartz and Hall (1971) have reported that a number of substituted bicyclobutanes can be homopolymerized and copolymerized to high molecular weight polymers. The bicyclobutanes which gave the best results were those with electronegative substituents (COOH, COOR, $CONH_2$, $COCH_3$, CN) at the bridgehead.



To extend this work to other bicyclic systems containing strained C-C single bonds, the nortricyclene system was explored. 1-Acetylnortricyclene (1) and 1-nortricyclenecarbonitrile (2) were synthesized and

several attempts were made to homopolymerize and copolymerize 1-acetylnortricyclene.



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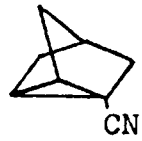

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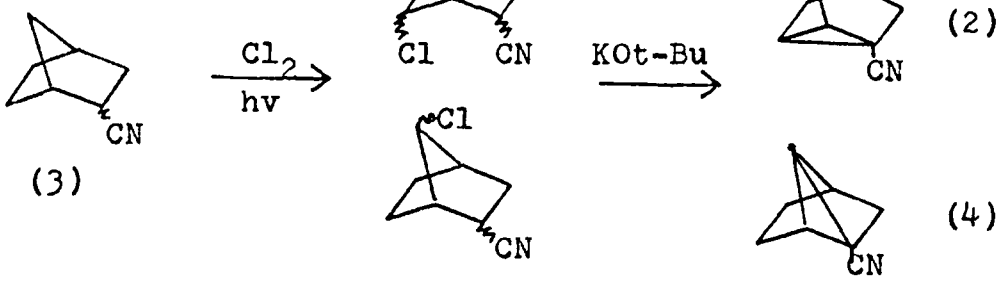
It was desired to prepare 1-nortricyclenecarbonitrile (2) in order to compare it with a nitrile previously prepared by Hall (unpublished work). In the procedure of Hall, chlorination of 2-norbornanecarbonitrile (3) gave only one product, but it was uncertain whether chlorination had occured at the 6 or 7 position. Therefore it was uncertain whether (2) or (4) had been obtained on treatment of the chloro compound with potassium t-butoxide.

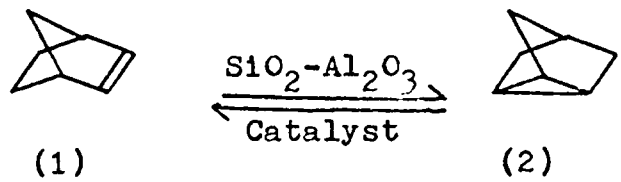


(3)

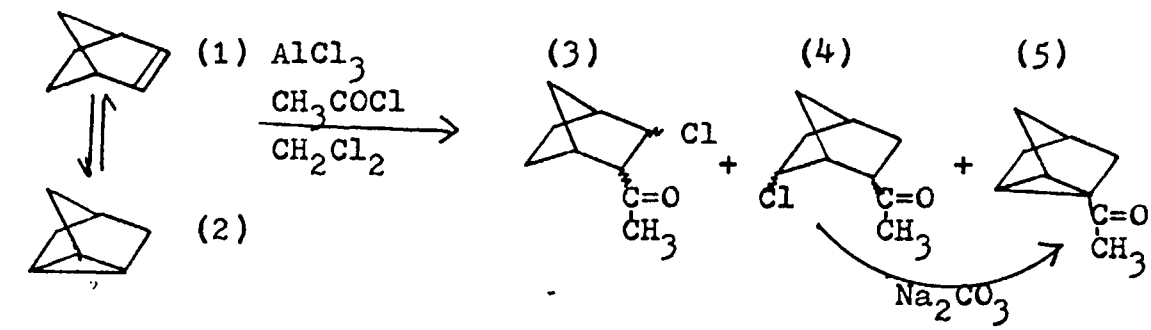
In this work, 1-nortricyclenecarbonitrile (2) was prepared by another method and compared to the product obtained by Hall.

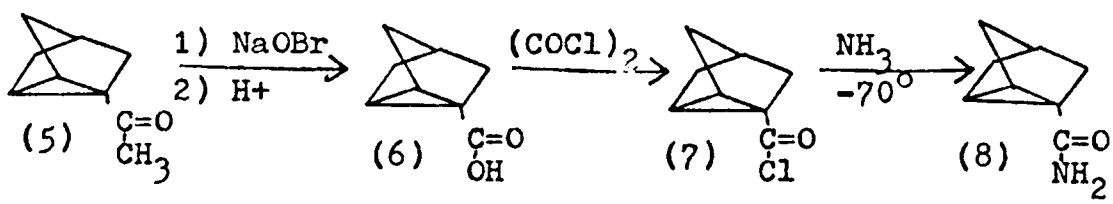
RESULTS AND DISCUSSION

Nortricyclene (2) was prepared by isomerization of norbornene (1). The procedure followed was that of Schleyer (1958), in which norbornene was refluxed over a silica-alumina catalyst and distilled. This resulted in an equilibrium mixture consisting of 29% norbornene (1) and 71% nortricyclene (2).

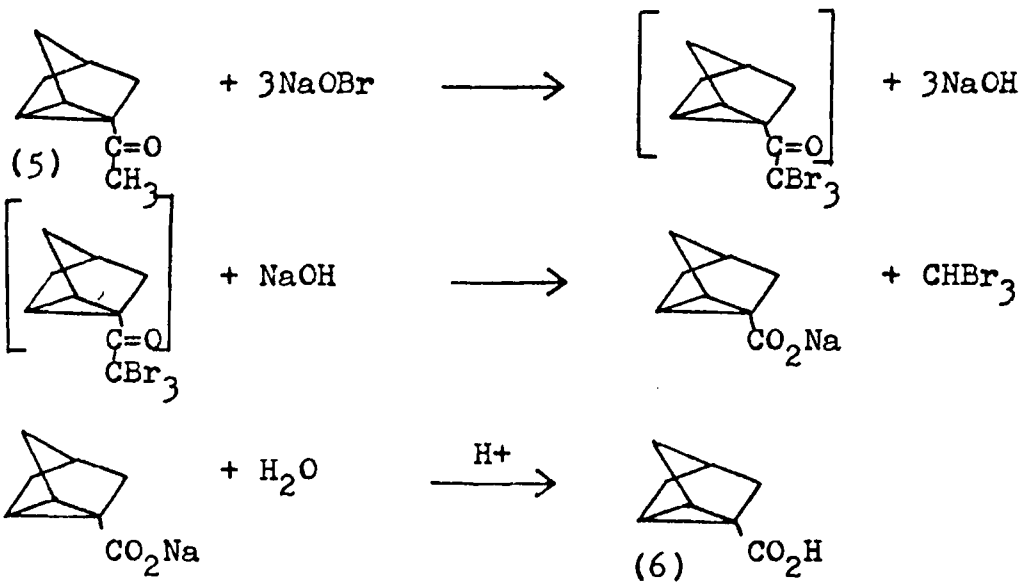


The equilibrium mixture was converted to 1-acetyl-nortricyclene (5) and then to 1-nortricyclenecarboxamide (8) as shown below. This was the procedure of Hart and Martin (1959).



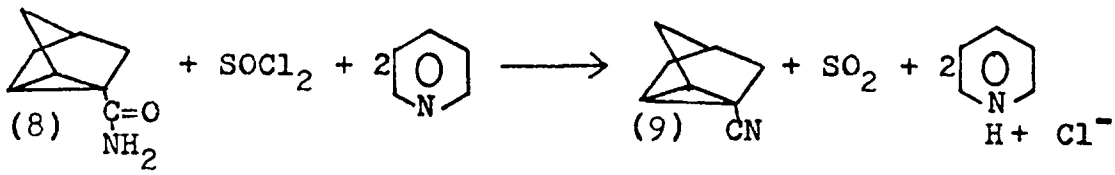


Treatment of the equilibrium mixture with aluminum chloride and acetyl chloride in methylene chloride gave three products: 2-chloro-3-acetylnorbornane (3), resulting from addition of acetyl chloride to the double bond of norbornene (1); 2-chloro-6-acetylnorbornane (4), resulting from addition of acetyl chloride across the cyclopropane ring of nortricyclene (2); and 1-acetylnortricyclene (5), the Friedel-Crafts product. 2-Chloro-6-acetylnorbornane (4) was converted to 1-acetylnortricyclene (5) by refluxing with sodium carbonate. An attempt was also made to use triethylamine in place of sodium carbonate, but this was unsuccessful. 1-Acetyl nortricyclene (5) was converted to 1-nortricyclenecarboxylic acid (6) by the haloform reaction.

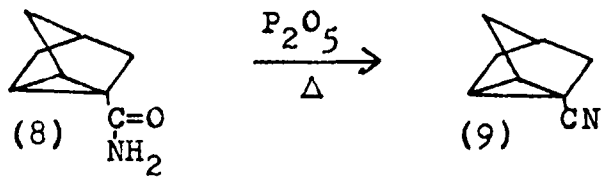


Treatment of the acid with either thionyl chloride or oxalyl chloride readily gave 1-nortricyclenecarbonyl chloride (7). 1-Nortricyclenecarboxamide (8) was obtained by treatment of the acid chloride with liquid ammonia. Its melting point agreed with that given by Hart and Martin.

Attempts to prepare 1-nortricyclenecarbonitrile (9) from 1-nortricyclenecarboxamide (8) by reaction with thionyl chloride and pyridine proved unsuccessful.



The nitrile was successfully prepared by dehydration of the amide with phosphorus pentoxide.



The compound obtained was shown by ir, nmr and vpc to be identical to the compound prepared by Hall in every respect. Therefore chlorination of 2-norbornanecarbonitrile had occured at the 6 position.

The acetyl compound being most readily available, was subjected to the following polymerization conditions:

The monomer was heated with a small amount of metallic sodium to 200°. The solution turned brown, but no polymer formed. After three hours, there was no sodium left in the reaction vessel and no gas was evolved on addition of methanol. It seems likely that the sodium may have reacted with the enol of 1-acetylnortricyclene.

In another experiment, 1-acetylnortricyclene was heated to 200° with a catalytic amount of di-t-butyl peroxide. Again the solution turned brown, but no polymer formed.

When 1-acetylnortricyclene and styrene were mixed with a catalytic amount of azobisisobutyronitrile (AIBN) in a sealed tube and heated to 60° overnight, a solid plug formed. The polymer was dissolved in benzene, precipitated in methanol, and a film of the polymer prepared. However, an infrared spectrum of this film showed only polystyrene.

An anionic copolymerization of 1-acetylnortricyclene and styrene was also tried using sodium-naphthalene as initiator. As in the free radical case, the polymer obtained was shown by ir to be polystyrene.

An attempt was also made to copolymerize 1-acetylnortricyclene and vinyl chloride. The procedure used was that of Sorenson and Campbell (1968, p. 227) for

emulsion polymerization with potassium persulfate as initiator. As before, the polymer obtained was shown by ir not to contain any 1-acetylnortricyclene.

It must be concluded that bridgehead-substituted nortricyclenes are reluctant to polymerize. Evidently, not enough additional strain is added to the cyclopropane ring by the nortricyclene system to encourage polymerization.

EXPERIMENTAL

Norbornene (Union Carbide) was distilled from sodium. Styrene (Matheson, Coleman and Bell) was purified by vacuum distillation and stored under nitrogen in a Dry Ice box. Tetrahydrofuran (Mallinckrodt) was distilled from lithium aluminum hydride. Naphthalene (Matheson, Coleman and Bell) was purified by sublimation. Sodium (Mallinckrodt), di-t-butyl peroxide (Matheson, Coleman and Bell), azobisisobutyronitrile (DuPont), potassium persulfate (Mallinckrodt), ORR soap (sodium stearate, sodium oleate and sodium palmitate) (Proctor and Gamble), vinyl chloride (Matheson), and other chemicals were used without further purification.

Nuclear magnetic resonance (nmr) spectra were determined on either a Varian model A-60 spectrometer at 60 MHz or on a Varian model HA-100 spectrometer at 100 MHz using tetramethylsilane as an internal standard. Infrared (ir) spectra were obtained with a Perkin-Elmer 337 grating infrared spectrophotometer. A polystyrene film was used to calibrate the instrument. Vapor phase chromatography (vpc) was carried out on a Varian Aerograph series 1700 with a 5 foot 3% SE-30 Verapore 30/120 mesh column and a Leeds and Northrup speedomax H recorder.

Melting points were determined on a Mettler Mel-temp apparatus. Inherent viscosities were determined with an Ostwald-Fenske viscometer. The concentration of all solutions was 0.1 g per dl with solvents as indicated.

Nortricyclene

The procedure of Schleyer (1958) was used. Norbornene (240 g, 2.52 mol) was purified by distillation from sodium and was then refluxed over 2.0 g of crushed silica-alumina catalyst (Houdry code 24 CP-15) for two hours. The isomerization was followed by vapor phase chromatography. This resulted in an equilibrium mixture consisting of 71% nortricyclene and 29% norbornene. Continued refluxing resulted in polymerization. When isomerization was complete, the mixture was distilled; yield, 133.2 g (55.5%).

1-Acetylnortricyclene

The procedure of Hart and Martin (1959) was used. Anhydrous aluminum chloride (77.2 g, 0.58 mol) was added to 200 ml of methylene chloride in a flask. Acetyl chloride (50.0 g, 0.64 mol) in 100 ml of methylene chloride was added dropwise for 1.5 hours to the aluminum chloride solution. The mixture was stirred constantly and the temperature maintained at approximately 5° with an ice water bath. The solution was stirred for one

hour until it became clear. The nortricyclene-norbornene mixture (55.4 g, 0.58 mol) in 152 ml of methylene chloride was added dropwise to this solution at 5° for 1.5 hours. The mixture was stirred for 15 more minutes at 5° and then warmed for 1.25 hours with stirring to room temperature.

A 20% hydrochloric acid solution (400 ml) was added dropwise to destroy the remaining aluminum chloride and acetyl chloride. A gray precipitate formed at first, but it redissolved as more hydrochloric acid was added. The layers were separated. The water layer was extracted twice with 100 ml portions of methylene chloride. The combined organic layers were then washed twice with 100 ml of water, twice with 100 ml of saturated sodium bicarbonate solution, once more with 100 ml of water, and dried overnight over magnesium sulfate. The methylene chloride was boiled off under aspirator pressure and the resultant yellow oil redissolved in benzene. The benzene was then distilled away to remove all of the methylene chloride; yield, 69.6 g of yellow oil.

Sodium carbonate monohydrate (74.4 g, 0.76 mol) in 375 ml of water was heated to reflux with mechanical stirring. The above oil (52.2 g) was added dropwise for 30 minutes. The resulting heterogeneous mixture was refluxed and stirred for 15 minutes more and then

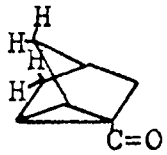
the layers were separated. The water layer was extracted twice with 90 ml of diethyl ether and the combined organic layers dried overnight over magnesium sulfate. The aqueous layer was acidified with nitric acid and silver nitrate was added to test for chloride ion. A white precipitate of silver chloride was obtained indicating that sodium carbonate had been successful in eliminating HCl from 2-chloro-6-acetylnorbornane to give 1-acetylnortricyclene.

The brown organic solution was distilled under full vacuum pump. It yielded a colorless liquid. Vapor phase chromatography showed one major peak, assigned to 1-acetylnortricyclene, one lower boiling impurity, and two higher boiling impurities presumed to be 2-chloro-6-acetylnorbornane and 2-chloro-3-acetyl-norbornane. Two other low boiling impurities were also present, but their peaks were very small. It was thought that one of these lower boiling compounds might be 2-acetylnorbornene, resulting from elimination of HCl from 2-chloro-3-acetylnorbornane, but an nmr spectrum (neat) showed no vinyl protons.

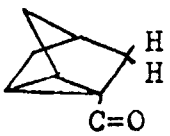
The crude 1-acetylnortricyclene from several preparations (80 ml) was fractionated through a spinning band column at 2 mm. This resulted in 7 ml of a low boiling fraction with considerable amounts of the low

boiling impurity, 30 ml of a medium boiling fraction, approximately 95% 1-acetylnortricyclene, and 40 ml of a high boiling fraction, rich in high boiling impurities. The middle fraction from above was further fractionated through a glass helices packed column into five fractions varying in degree of purity. The third fraction was better than 99% pure 1-acetylnortricyclene. The high and low boiling fractions from the spinning band fractionation were combined and refractionated through the glass helices packed column into six fractions. The high boiling impurities were completely eliminated from these fractions.

The infrared spectrum of the purified 1-acetylnortricyclene (neat) clearly indicated the presence of the cyclopropane carbon-hydrogen stretch at 3060 cm^{-1} and of the carbonyl stretch located α to the cyclopropane ring at 1675 cm^{-1}. The nmr spectrum (neat) showed a singlet (integration 4) at 8.55 T due to

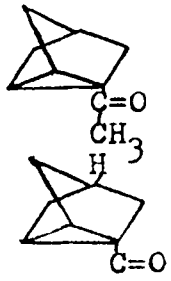


, a doublet (integration 2) at 8.43 T due to



, a singlet (integration 2) at 8.02 T due to

, a singlet (integration 3) at 7.94 T due to



, and a multiplet (integration 1) at 7.84 T due to

.

1-Nortricyclenecarboxylic acid

The procedure of Hart and Martin (1959) was used. The acid was prepared from 1-acetylnortricyclene using the haloform reaction. Bromine (7.56 ml, 0.14 mol) was added dropwise to 18.9 g (0.47 mol) of sodium hydroxide in 126 ml of water at 0° with stirring. This resulted in a yellow solution of sodium hypobromite. The yellow solution was added dropwise to 6.30 g (0.05 mol) of 1-acetylnortricyclene. The mixture was stirred at 0° for 30 minutes and then at room temperature for 3 hours. The color slowly changed from yellow to colorless.

The colorless solution was acidified with dilute hydrochloric acid until a white precipitate of 1-nortricyclenecarboxylic acid formed. Sodium bisulfite was added to destroy any excess bromine.

$$NaHSO_3 + Br_2 + H_2O \longrightarrow NaHSO_4 + 2HBr$$

The aqueous solution was extracted three times with diethyl ether in which the acid dissolved and the combined ether layers were extracted three times with 10% sodium hydroxide. The aqueous layers were combined and

acidified with hydrochloric acid. The resulting white precipitate was filtered off; yield, 4.7 g of the crude acid, mp 112-114° (lit. mp 119-120°, Hart and Martin, 1959). The crude acid was recrystallized from diethyl ether at -80°; yield, 2.90 g (40%).

The infrared spectrum of the acid in chloroform showed a broad OH absorption above 3000 cm^{-1} and a strong carbonyl absorption at 1665 cm^{-1}.

1-Nortricyclenecarboxamide

The procedure of Hart and Martin (1959) was used. 1-Nortricyclenecarboxylic acid (2.31 g, 0.017 mol) was dissolved in diethyl ether and added dropwise to 3.0 ml (50% excess) of oxalyl chloride, to form the acid chloride. The mixture was stirred until evolution of gas ceased. It was then warmed to reflux for a few minutes to insure that the reaction was complete and filtered. The solvent was removed on a rotary evaporator leaving a yellow oil.

The infrared spectrum (neat) showed cyclopropane carbon-hydrogen stretch at 3055 cm^{-1} and carbonyl stretch at 1775 cm^{-1}.

1-Nortricyclenecarbonyl chloride was dissolved in diethyl ether and added dropwise to excess liquid ammonia. The mixture was warmed to room temperature and the white crystals were washed with water to remove

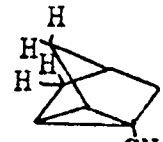
ammonium chloride. The remaining crystals were dissolved in hot ethanol and the solution was evaporated to dryness on a rotary evaporator; yield, 1.4 g (61%), mp 222-225° dec. (lit. mp 219-222° dec., Hart and Martin, 1959). Recrystallization was unnecessary.

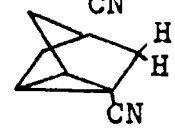
The infrared spectrum of the amide in a KBr pellet showed nitrogen-hydrogen stretch at 3350 cm^{-1} and 3175 cm^{-1}, nitrogen-hydrogen bend at 1620 cm^{-1}, and carbonyl stretch at 1665 cm^{-1}.

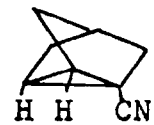
1-Nortricyclenecarbonitrile

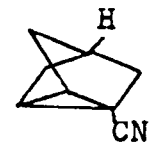
1-Nortricyclenecarboxamide (1.4 g, 0.01 mol) was placed in a test tube connected to a cold trap and mixed with an excess of phosphorus pentoxide. The cold trap was placed in a Dry Ice-acetone bath and the test tube was heated with a bunsen burner under full vacuum pump, until the material in the tube turned black. The cold trap yielded a solid which formed a liquid when warmed to room temperature. The liquid was taken up in diethyl ether and dried over molecular sieves. The solvent was removed by rotary evaporation leaving a yellow oil, which proved to be the nitrile.

The infrared spectrum (neat) showed cyclopropane carbon-hydrogen stretch at 3075 cm^{-1} and carbon-nitrogen stretch at 2240 cm^{-1}. The nmr spectrum (neat) showed a

singlet at 8.65 T (integration 4) due to  ,

a singlet at 8.52 T (integration 2) due to  ,

a singlet at 8.21 T (integration 2) due to  ,

and a singlet at 7.93 T (integration 1) due to  .

The ir and nmr spectra and the vpc retention time were identical in every respect to Hall's material (unpublished work).

Attempted Homopolymerization of 1-Acetylnortricyclene

1-Acetylnortricyclene (3 ml) was placed in a test tube and the test tube flushed with nitrogen. A small chunk of metallic sodium was added and the test tube heated to 200° under nitrogen. After 3 hours the resulting yellow-brown solution was cooled to room temperature. Methanol was then added. There was no sodium left in the bottom of the test tube, and no gas was released upon addition of methanol. No precipitate of polymer was observed and vapor phase chromatography of the methanol solution showed only two peaks, presumably due to the methanol and to the 1-acetylnortricyclene.

1-Acetylnortricyclene (3 ml) was placed in a test tube with 3 drops of di-t-butyl peroxide and heated under nitrogen slowly to 200°. The liquid turned brown, but no polymer formed.

Attempted Free Radical Copolymerization of 1-Acetylnortricyclene and Styrene

To 0.75 ml of styrene in a test tube was added 10 mg of azobisisobutyronitrile. The tube was evacuated, sealed and heated overnight to 65°. A solid plug formed. The plug was dissolved in benzene and precipitated in excess methanol. It was blended and filtered. The white powder was dissolved in benzene, precipitated in methanol, blended, and filtered again; yield, 0.35 g. The above procedure was repeated with 0.25 ml of 1-acetylnortricyclene added; yield, 0.35 g.

Films of the above two polymers were prepared and the infrared spectra compared. The spectra were identical and no carbonyl absorption was observed. Evidently the 1-acetylnortricyclene was not incorporated into the polymer.

Using a viscometer in an oil bath at 32°, the inherent viscosities of the two polymers were determined in benzene. The inherent viscosity of the polymer prepared in the absence of 1-acetylnortricyclene was 0.58 and the inherent viscosity of the polymer prepared in the presence of 1-acetylnortricyclene was 0.39.

Attempted Anionic Copolymerization of 1-Acetylnortricyclene and Styrene

Tetrahydrofuran (50 ml) was refluxed under nitrogen to remove oxygen. Naphthalene (1 g, 7.8 mmol) and 0.18 g (7.8 mmol) of sodium were added to the tetrahydrofuran. The mixture was stirred for 2 hours giving a green solution.

A 25 ml test tube was flamed out under nitrogen and fitted with a three way stopcock. The nitrogen was first passed through sulfuric acid and then through reduced copper oxide in order to remove all water and oxygen. Oxygen-free tetrahydrofuran (20 ml) was placed in the tube. The initiator solution was added dropwise until the solution turned green. The test tube was then cooled in an ice water bath. Styrene (1.5 ml) was then added. The solution turned colorless. At ice bath temperature, more initiator was added until the solution turned wine red indicating the presence of the styryl anion. The solution was left under positive nitrogen pressure overnight. By the next morning, the solution was again colorless. It was poured into methanol and the polystyrene precipitated. The polymer was then blended and filtered; yield, 1.26 g.

1-Acetylnortricyclene (0.25 ml) was added to a 25 ml test tube fitted with a three way stopcock. It was degassed and covered with nitrogen. Oxygen-free

tetrahydrofuran (10 ml) was added followed by 0.75 ml of styrene. The initiator solution was then added dropwise until the red color of the styryl anion persisted. The test tube was left overnight under positive nitrogen pressure. By the next morning, the solution was again colorless. It was poured into methanol and the polymer precipitated. The polymer was then blended and filtered; yield, 0.35 g.

Films of the above two polymers were prepared and the infrared spectra compared. The spectra were identical and no carbonyl absorption was observed. Evidently the 1-acetylnortricyclene was not incorporated into the polymer.

Using a viscometer in an oil bath at 31°, the inherent viscosities of the two polymers were determined in benzene. The inherent viscosity of the polymer prepared in the absence of 1-acetylnortricyclene was 0.20 and the inherent viscosity of the polymer prepared in the presence of 1-acetylnortricyclene was 0.10.

Attempted Free Radical Copolymerization of 1-Acetylnortricyclene and Vinyl Chloride

The procedure of Sorenson and Campbell (1968, p. 227) was used. A 0.5% soap solution was prepared by dissolving 0.5 g of ORR soap in 100 ml of oxygen-free water (refluxed under nitrogen). The soap solution

(30 ml) and 0.08 g of potassium persulfate were added to a thick-walled bottle of 250 ml capacity. The mixture was frozen in a Dry Ice-acetone bath and 10 g of vinyl chloride dripped in through a Dry Ice condenser. The bottle was sealed with a bottle cap, warmed to 50° in a water bath and stirred overnight. A milky white emulsion resulted. The bottle was cooled in a Dry Ice-acetone bath, opened, and warmed to room temperature. The polymer was then precipitated in a sodium chloride solution. The poly(vinyl chloride), a white powder, was filtered off, washed several times with hot water to remove excess soap, washed with methanol, dissolved in tetrahydrofuran, filtered, precipitated in methanol, blended, and filtered; yield, 3.7 g. The above procedure was repeated with 3 g of degassed 1-acetylnortricyclene added; yield, 3.3 g.

Films of the above two polymers were prepared and the infrared spectra compared. The spectra were identical and no carbonyl absorption was observed. Evidently the 1-acetylnortricyclene was not incorporated into the polymer.

Using a viscometer in an oil bath at 31°, the inherent viscosities of the two polymers were determined in tetrahydrofuran. The inherent viscosity of the polymer prepared in the absence of 1-acetylnortricyclene was

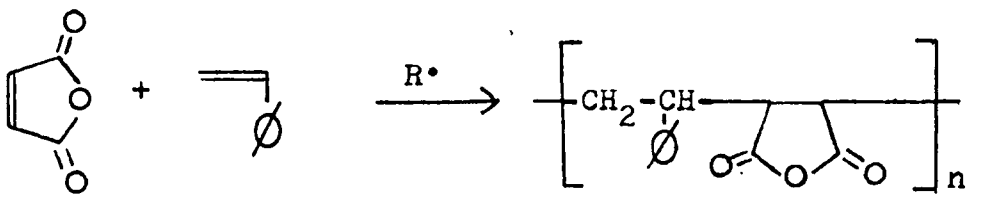
0.39 and the inherent viscosity of the polymer prepared in the presence of 1-acetylnortricyclene was 0.58.

PART II

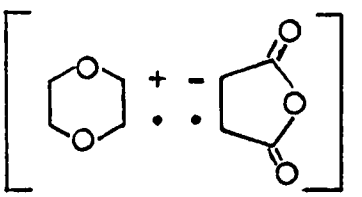
1:1 ALTERNATING COPOLYMERS OF BICYCLOBUTANES

INTRODUCTION

Certain 1:1 alternating copolymers have been known for many years. These result from the copolymerization of electron-rich monomers with electron-poor monomers. An example of this is the free radical copolymerization of maleic anhydride and styrene.

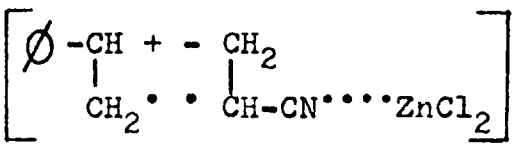


Other examples are the copolymerization of sulfur dioxide and ∝ olefins and the copolymerization of p-dioxene or vinyl ethers and maleic anhydride. In the latter case, Iwatsuki and Yamashita (1965) have proposed the formation of a charge-transfer complex to explain why alternating copolymers are obtained.



In recent years, some success has been had in inducing formation of 1:1 alternating copolymers by complexing electron-poor monomers, such as acrylonitrile, methacrylonitrile, methyl acrylate, or methyl methacrylate with a metal halide such as zinc chloride or

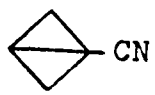
aluminum sesquichloride to make it even more electrophilic and copolymerizing with an electron-rich monomer, such as styrene, butadiene, or isoprene. Such polymerizations can be carried out with or without the presence of a free radical initiator. A good review of this method has been given by Gaylord (1970). The mechanism proposed by Gaylord and Takahashi (1968) to explain why alternating copolymers are obtained involves formation of a donor-acceptor complex followed by homopolymerization of this complex. In these polymerizations,



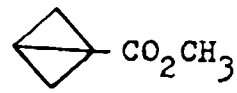
high molecular weight 1:1 copolymers are obtained regardless of the monomer feed ratio. Hence, the polymers are assumed to be alternating. In the case of poly(methyl methacrylate-co-styrene) prepared in this way, more definitive proof that the polymer formed is indeed alternating can be obtained via nmr (Ito and Yamashita, 1965 and Hirooka et al., 1968). Although equimolar copolymers are obtained at low temperatures and low conversions, when the temperature is raised or when polymerization is carried to high conversion, a non-equimolar polymer results. Takahashi and Gaylord (1970) attribute this to the formation of homopolymer or randon

copolymer simultaneously with, but at different rates from the formation of the alternating copolymer. In some cases, the alternating copolymer can be separated from the non-alternating copolymer by fractionation (Gaylord and Antropiusova, 1970).

Since Hall et al. (1971a,-b) and Swartz and Hall (1971) have found that bicyclobutanes polymerize in a similar manner to their vinyl analogs, it was desired to see if they could also be made to form 1:1 alternating copolymers as the corresponding vinyl monomers do. In this work, 1:1 copolymers were made from 1-bicyclobutanecarbonitrile (1) and styrene and from methyl 1-bicyclobutanecarboxylate (2) and styrene, using zinc chloride as the complexing agent. In the case of 1-bicyclobutanecarbonitrile and styrene, the polymer was shown to be alternating by varying the monomer feed ratios and observing the amount of each monomer in the copolymer.



(1)



(2)

RESULTS AND DISCUSSION

Preliminary Experiments with Vinyl Monomers in Bulk

Several Copolymerizations of acrylonitrile and other olefins with Lewis acids were attempted in order to gain experience with this type of polymerization. The attempted copolymerization of acrylonitrile and 1-hexene in bulk with an equivalent of boron trifluoride and azobisisobutyronitrile at room temperature yielded no polymer. Apparently, 1-hexene was too unreactive to be copolymerized. The attempted copolymerization of acrylonitrile and styrene in bulk with an equivalent of boron trifluoride and azobisisobutyronitrile at room temperature was also unsuccessful, yielding only polystyrene, perhaps by a cationic mechanism. Copolymerization of acrylonitrile and styrene in bulk with an equivalent of zinc chloride was successful. The method used was that of Yabumoto, Ishii and Arita (1969). The nmr spectrum of the polymer indicated that it contained more acrylonitrile than styrene, but since the polymerization was carried to full conversion, this was to be expected.

Polymerizations of Bicyclobutanes in Bulk

The above procedure for acrylonitrile, styrene and zinc chloride was applied to the copolymerization

of 1-bicyclobutanecarbonitrile and styrene in bulk with an equivalent of zinc chloride at room temperature. A few mg of benzoyl peroxide were also added. The polymer obtained was insoluble in all solvents tried. However, elemental analysis of the polymer indicated that 1-bicyclobutanecarbonitrile and styrene were present in equimolar amounts.

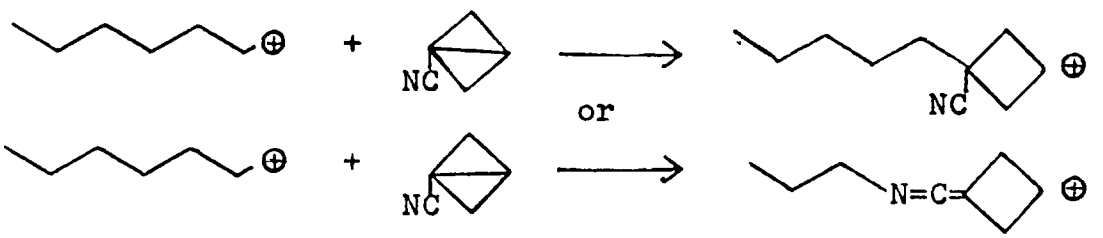
To establish that monomers other than styrene could be used, 1-bicyclobutanecarbonitrile and vinyl butyl ether were copolymerized in bulk. A catalytic amount of zinc chloride produced no polymer, but when a full equivalent of zinc chloride was used, polymer formed. The polymer was soluble in N-methylpyrrolidone after sodium methoxide in methanol was added. It was precipitated by addition to methanol. An nmr spectrum showed that the vinyl butyl ether had been incorporated into the polymer.

A copolymer of methyl 1-bicyclobutancarboxylate and styrene prepared in bulk with a catalytic amount of zinc chloride was soluble in chloroform, but a copolymer prepared in bulk with a full equivalent of zinc chloride was mostly insoluble.

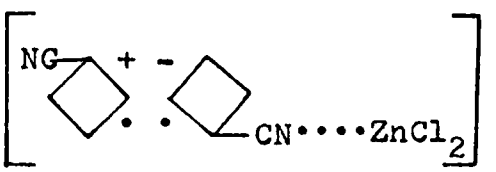
A number of homopolymerizations were also carried out. 1-Bicyclobutanecarbonitrile was homopolymerized

with a catalytic amount of zinc chloride. Most of the resulting polymer was insoluble in all solvents tried. An infrared spectrum of the small amount that was soluble showed evidence for both CN and C=C=N. The polymerization was repeated with a full equivalent of zinc chloride. This polymer was insoluble in all solvents tried.

The fact that 1-bicyclobutanecarbonitrile polymerized with zinc chloride in the absence of a free radical initiator could indicate a cationic polymerization. This could theoretically lead to two types of linkages in the polymer, both of which were observed in the infrared spectrum.

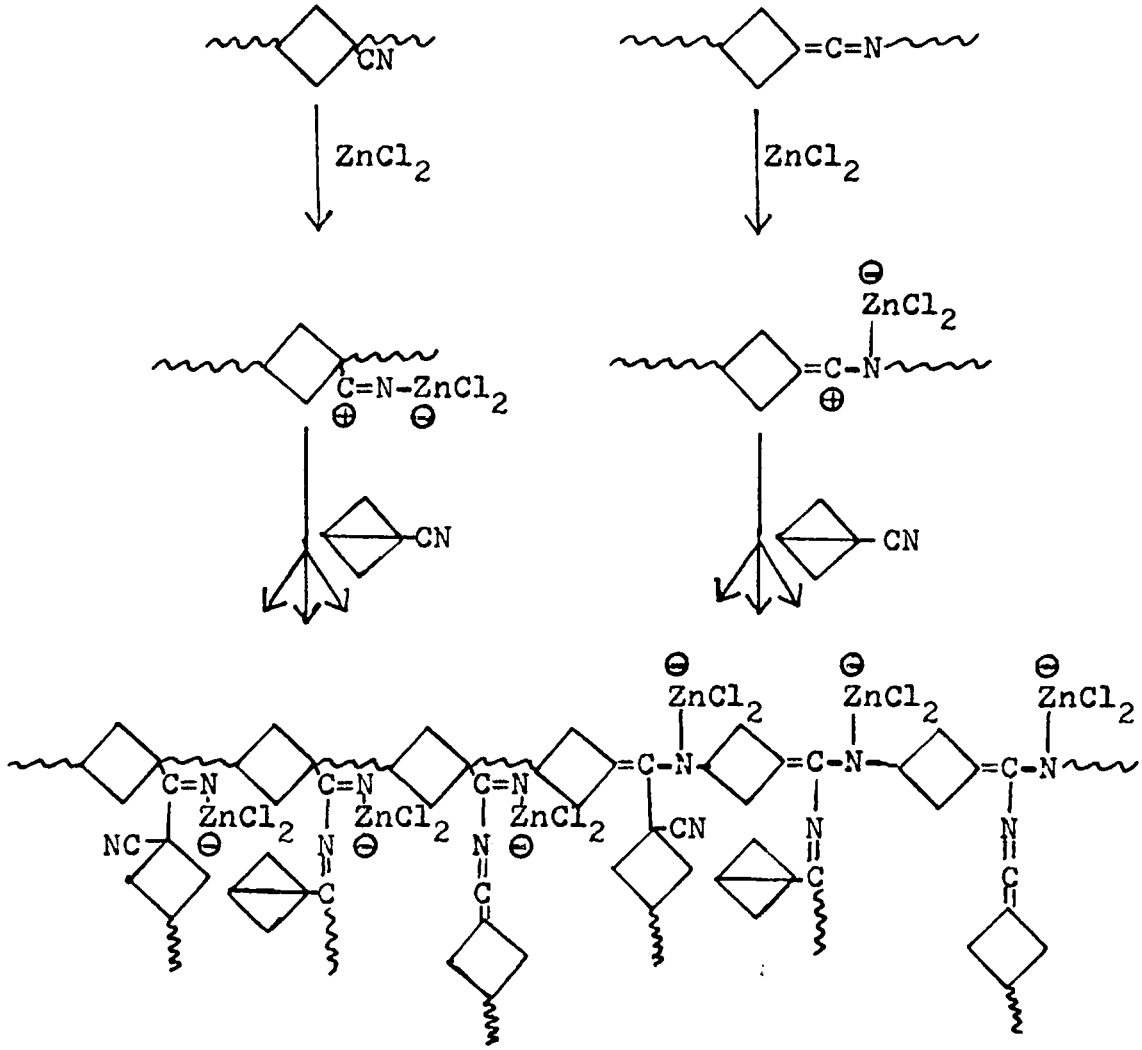


An alternative mechanism could involve formation of a charge-transfer complex followed by spontaneous polymerization as has been suggested for the homopolymerization of acrylonitrile (Gaylord and Takahashi, 1968).

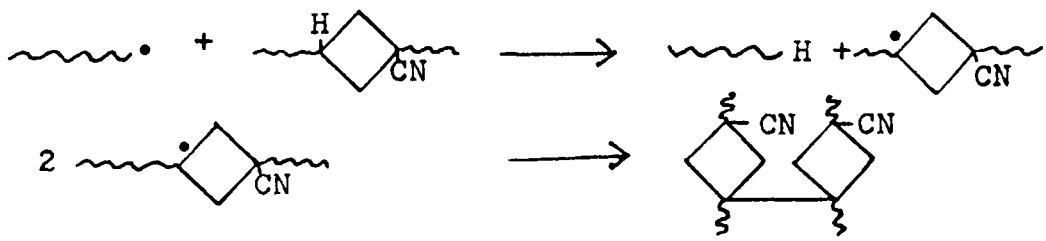


This mechanism, however, fails to explain the presence of ketenimine linkages in the polymer.

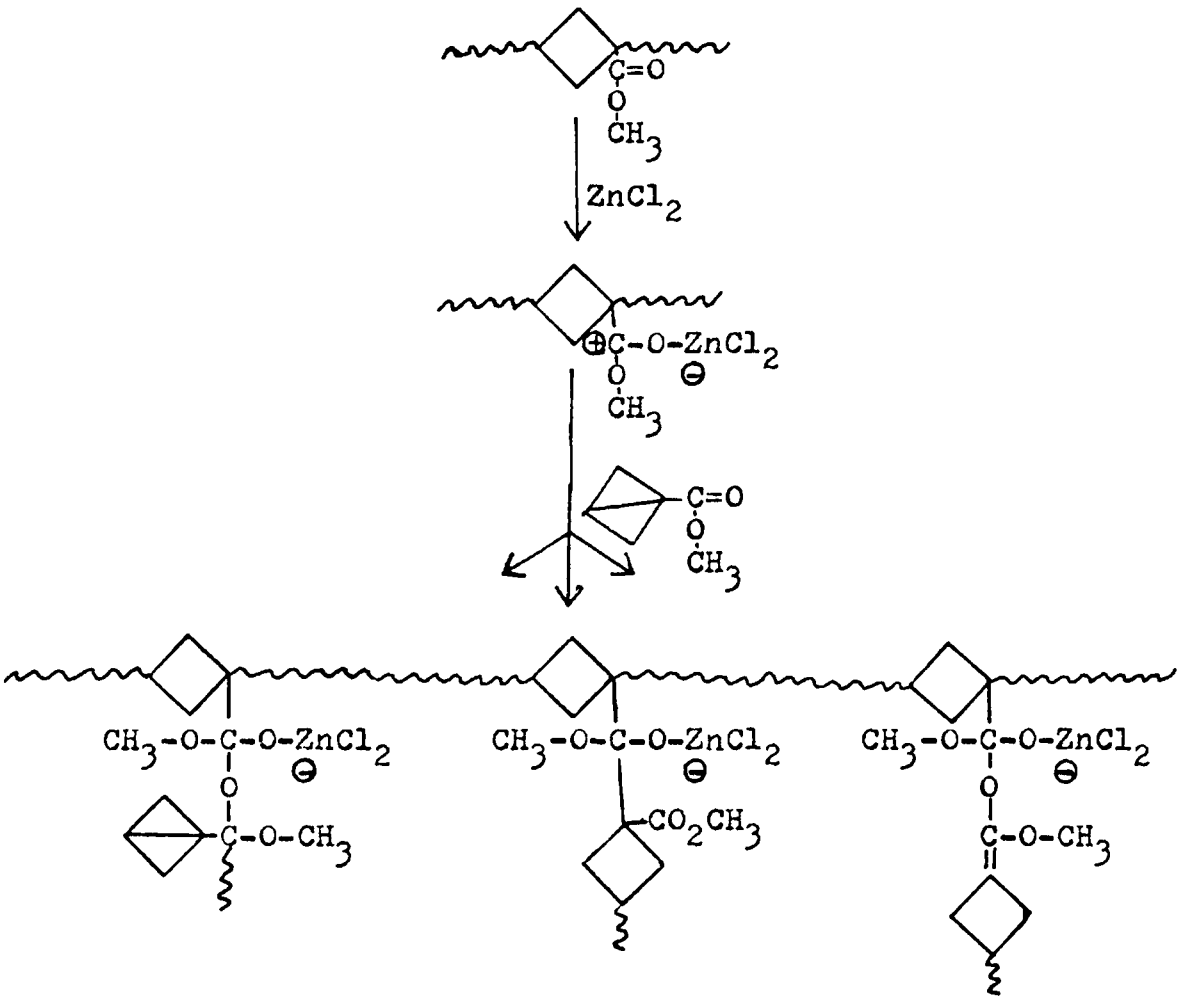
The inability to find a solvent for the homopolymer or the copolymer suggests that they may be crosslinked or highly branched. The following mechanisms could be possible:

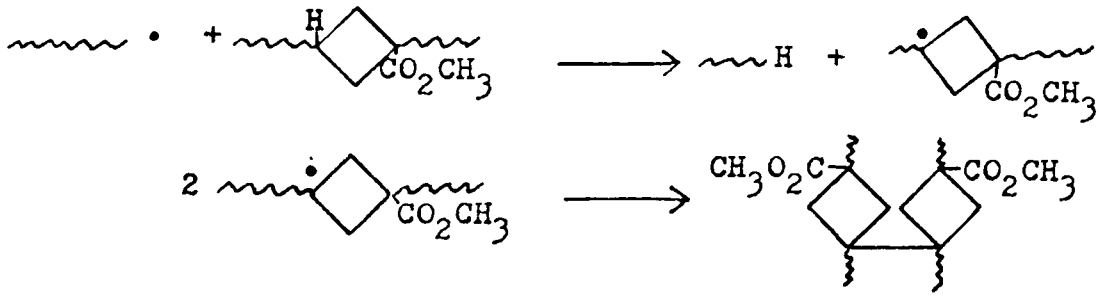


A free radical mechanism might also be invoked to explain the observed crosslinking.



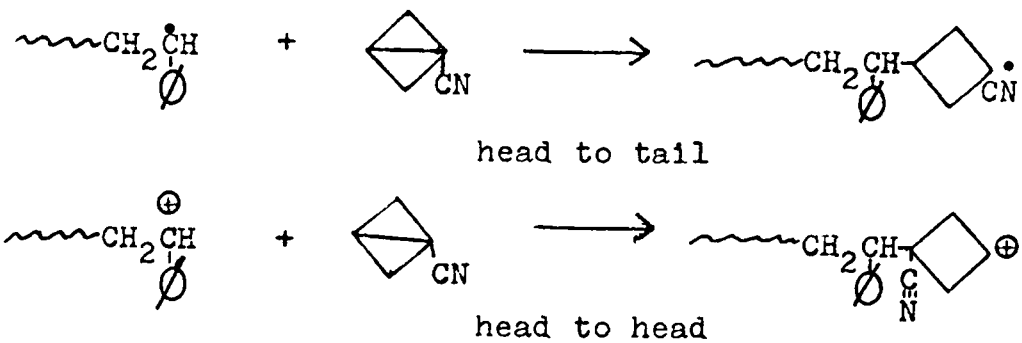
Methyl 1-bicyclobutanecarboxylate was homopolymerized with a catalytic amount of zinc chloride and with a full equivalent of zinc chloride. In both cases, most of the polymer remained insoluble. This could be explained, as in the case of 1-bicyclobutanecarbonitrile, in terms of branching via a cationic mechanism or by crosslinking via a free radical mechanism.





A summary of the above results is presented in Table 1. Where zinc chloride is listed as a reactant, a full equivalent was used. Where it is on the arrow, a catalytic amount was used.

One way to resolve the mechanism problem would be to determine whether the monomers in the copolymer of 1-bicyclobutanecarbonitrile and styrene are connected head to head or head to tail. If the mechanism is either free radical or complex, one would expect head to tail linkages, but if the mechanism is cationic, one would expect head to head linkages. This has not yet been explored.



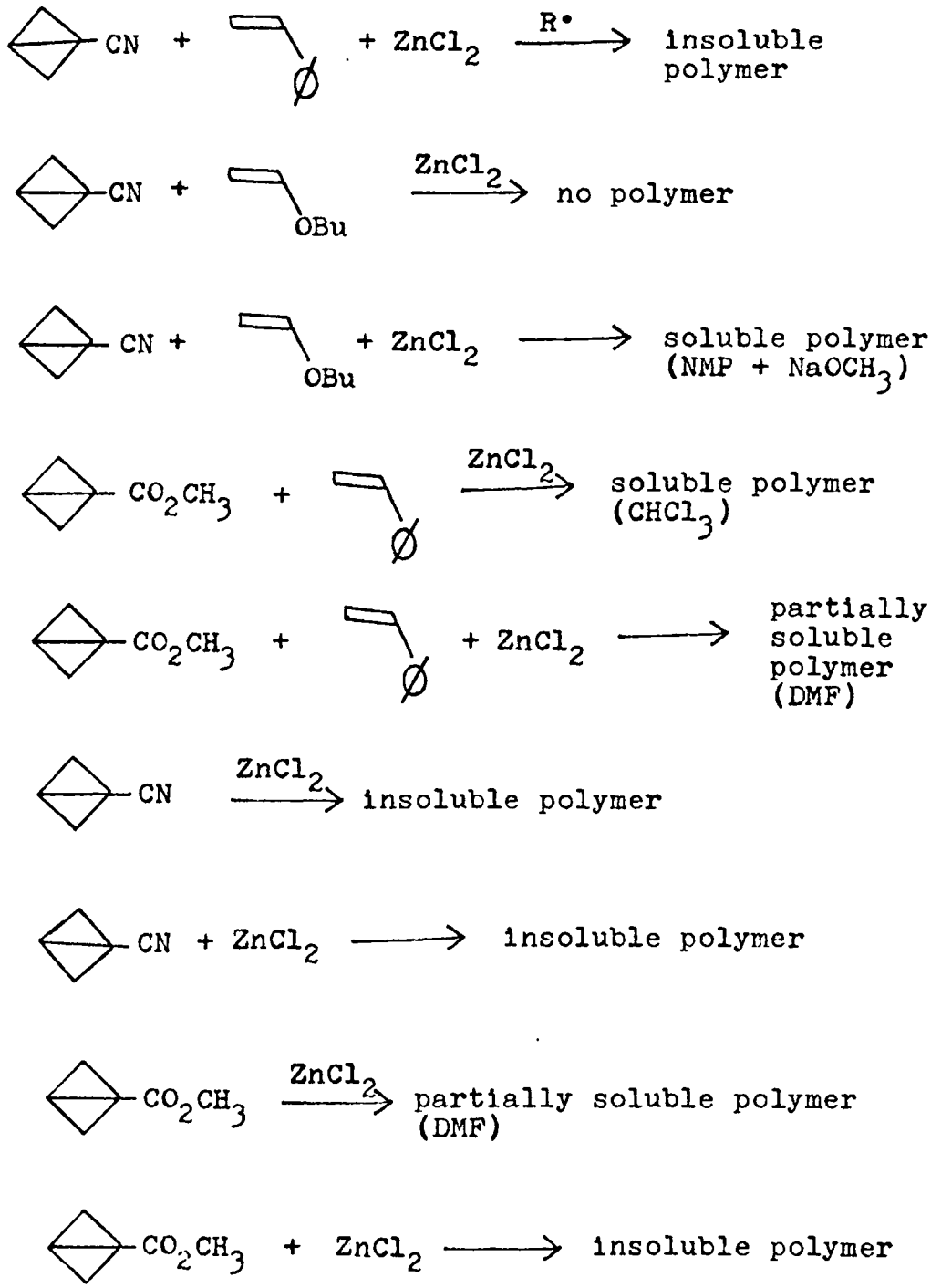
head to tail

head to head

Polymerization of Bicyclobutanes in Solution

One logical way around the problem of insoluble polymers was to run the polymerizations in a solvent.

Table 1. Summary of Polymerizations in Bulk.



NMP=N-methylpyrrolidone DMF=Dimethylformamide

The solvent chosen was tetramethylenesulfone because of its remarkable inertness to active reagents and because of its excellent solvating properties for both monomers and polymers. Most of the following polymerizations were carried out with stirring such that the zinc chloride dissolved in the solvent. (In the previous polymerizations, especially when a full equivalent of zinc chloride was used, most of the zinc chloride precipitated yielding a heterogeneous mixture.) Free radical initiators were used when polymerizations proceeded slowly without them. Initiators were only necessary in three cases: copolymerization of 1-bicyclobutanecarbonitrile and styrene with a catalytic amount of zinc chloride, copolymerization of methyl 1-bicyclobutanecarboxylate and styrene with a catalytic amount of zinc chloride, and copolymerization of methyl 1-bicyclobutanecarboxylate and styrene with an equivalent of zinc chloride.

1-Bicyclobutanecarbonitrile and methyl 1-bicyclobutanecarboxylate were homopolymerized and copolymerized with styrene, using both a catalytic amount of zinc chloride and a full equivalent of zinc chloride. These polymerizations were carried out in tetramethylenesulfone. In all cases, soluble polymers were obtained. The results of these polymerizations are listed in Tables

2 and 3. It is interesting to note, as in the case of polymerization of acrylonitrile with zinc chloride (Gaylord, 1970), that a much higher molecular weight polymer of 1-bicyclobutanecarbonitrile was obtained with zinc chloride than with free radical initiation (Hall et al., 1971a).

In order to determine whether these zinc chloride induced polymerizations were proceeding by a free radical or cationic mechanism, homopolymers of 1-bicyclobutanecarbonitrile and copolymers of 1-bicyclobutanecarbonitrile and styrene were prepared with an equivalent of zinc chloride and with either 10% 1,3-dimethoxybenzene or 10% carbon tetrachloride added, in tetramethylenesulfone. If the mechanism were cationic, 1,3-dimethoxybenzene would be expected to act as a chain-transfer agent, thereby lowering the molecular weight of the polymer obtained. If the mechanism were free radical, carbon tetrachloride would be expected to act as a chain-transfer agent, thereby lowering the molecular weight of the polymer obtained. As can be seen from Tables 2 and 3, a lower inherent viscosity was obtained for the homopolymer with 1,3-dimethoxybenzene, but not with carbon tetrachloride. The small difference, however, is hardly conclusive evidence for a cationic mechanism. In the copolymers, no change in inherent viscosity

was observed for either the polymer prepared in the presence of 1,3-dimethoxybenzene or the polymer prepared in the presence of carbon tetrachloride. This lends support to a charge-transfer complex mechanism.

It can be seen from Table 3, that when 1-bicyclobutanecarbonitrile and styrene were copolymerized with an equivalent of zinc chloride in tetramethylenesulfone, a 1:1 copolymer was obtained. In order to see if 1:1 copolymers would be obtained at all monomer feed ratios, the following two polymerizations were carried out: 1-Bicyclobutanecarbonitrile/styrene/zinc chloride (1/3/1), and 1-bicyclobutanecarbonitrile/styrene/zinc chloride (3/1/3). The results are listed in Table 3. As can be seen in the 1/3/1 case, carried to less than 10% conversion, the copolymer contained more styrene than 1-bicyclobutanecarbonitrile (27.4% 1-bicyclobutanecarbonitrile), but in the 3/1/3 case, carried to 85% conversion, the polymer was approximately 1:1 (53.7% 1-bicyclobutanecarbonitrile). It may be concluded from these results that at monomer feed ratios between 50% and 75% 1-bicyclobutanecarbonitrile, a 1:1 essentially alternating copolymer is obtained. It is interesting to note that in the 1/1/1 case an equimolar copolymer was obtained even at 63% conversion, and in the 3/1/3 case an equimolar copolymer was obtained at 80% conversion (based on 1:1 copolymer). It is not possible

to carry the acrylonitrile-styrene-zinc chloride polymerization to such high conversion and still obtain an equimolar copolymer.

As can be seen from Tables 2 and 3, the inherent viscosities of most of the polymers prepared in solution is quite large. They are, for the most part, high molecular weight film-forming polymers.

An attempt was made to use ethylaluminum sesquichloride in place of zinc chloride in the copolymerization of 1-bicyclobutanecarbonitrile and styrene, but it was unsuccessful.

An attempt was made to homopolymerize 1-bicyclopentanecarbonitrile with an equivalent of zinc chloride using azobisisobutyronitrile as the initiator at 60°, but no polymer was obtained. When the polymerization was repeated with styrene present, only polystyrene was obtained.

Table 2. Summary of Homopolymerizations in Tetramethylenesulfone.

Monomers + Lewis Acid	Mole Ratio	Initiator	Chain Transfer Agent	Temp. C	Time	Analysis Calc'd*	Analysis Found**	η_{inh}	% Yield
BBCN/$ZnCl_2$	1:cat	None	None	R.T.	2 Days	75.92% C 6.37% H 17.71% N	75.37% C 6.35% H 18.28% N	5.77	33%
BBCN/$ZnCl_2$	1:1	None	None	R.T.	1 Day	75.92% C 6.37% H 17.71% N	75.28% C 6.37% H 18.35% N	5.82	88%
BBCN/$ZnCl_2$	1:1	None	DMB	R.T.	2 Days	75.92% C 6.37% H 17.71% N	75.59% C 6.49% H 17.92% N	4.88	~100%
BBCN/$ZnCl_2$	1:1	None	CCl_4	R.T.	2 Days	75.92% C 6.37% H 17.71% N	75.92% C 6.40% H 17.68% N	6.68	~100%
MBBC/$ZnCl_2$	1:cat	None	None	R.T.	3 Days	64.27% C 7.19% H 28.54% O	64.91% C 7.20% H 27.89% O	5.13	62%
MBBC/$ZnCl_2$	1:1	None	None	R.T.	3 Days	64.27% C 7.19% H 28.54% O	64.64% C 7.04% H 28.32% O	4.64	45%

BBCN=1-Bicyclobutanecarbonitrile
MBBC=Methyl 1-bicyclobutanecarboxylate
cat=Catalytic amount
DMB=1,3-Dimethoxybenzene
R.T.=Room temperature

*calculated for 1:1
**adjusted values (without $ZnCl_2$)

Table 3. Summary of Copolymerizations in Tetramethylenesulfone

Monomers + Lewis Acid	Mole Ratio	Initiator	Chain Transfer Agent	Temp. °C	Time	Analysis Calc'd*	Analysis Found**	η_{inh}	% Yield
BBCN/S/$ZnCl_2$	1:1:cat	Benzoyl Peroxide	None	60°	1 Week	85.20% C 7.15% H 7.64% N	86.20% C 7.16% H 6.64% N	0.95	90%
BBCN/S/$ZnCl_2$	1:1:1	None	None	R.T.	4 Days	85.20% C 7.15% H 7.64% N	85.27% C 7.00% H 7.73% N	2.23	63%
BBCN/S/$ZnCl_2$	1:3:1	None	None	R.T.	1 Day	85.20% C 7.15% H 7.64% N.	88.34% C 7.52% H 4.14% N	----	<10% based on 1:1
BBCN/S/$ZnCl_2$	3:1:3	None	None	R.T.	2½ Hrs	85.20% C 7.15% H 7.64% N	84.79% C 7.02% H 8.19% N	2.85	85% based on 1:1
BBCN/S/$ZnCl_2$	1:1:1	None	DMB	R.T.	2 Days	85.20% C 7.15% H 7.64% N	85.38% C 7.17% H 7.45% N	2.31	38%
BBCN/S/$ZnCl_2$	1:1:1	None	CCl_4	R.T.	2 Days	85.20% C 7.15% H 7.64% N	85.24% C 7.17% H 7.59% N	2.47	38%

BBCN=1-Bicyclobutanecarbonitrile
S=Styrene
cat=Catalytic amount
DMB=1,3-Dimethoxybenzene
R.T.=Room temperature

*calculated for 1:1
**adjusted values (without $ZnCl_2$)

Table 3. Continued

Monomers + Lewis Acid	Mole Ratio	Initiator	Chain Transfer Agent	Temp. °C	Time	Analysis Calc'd*	Analysis Found**	η_{inh}	% Yield
MBBC/S/$ZnCl_2$	1:1:cat	Benzoyl Peroxide	None	60°	3 Days	77.75% C 7.46% H 14.79% O	81.87% C 7.39% H 10.74% O	----	55%
MBBC/S/$ZnCl_2$	1:1:1	None	None	R.T.	3 Days			----	11%
MBBC/S/$ZnCl_2$	1:1:1	Benzoyl Peroxide	None	60°	4 Days	77.75% C 7.46% H 14.79% O	79.39% C 7.69% H 12.92% O	0.39	44%

MBBC=Methyl 1-bicyclobutanecarboxylate
S=Styrene
cat=Catalytic amount
R.T.=Room temperature

*calculated for 1:1
**adjusted values (without $ZnCl_2$)

EXPERIMENTAL

1-Bicyclobutanecarbonitrile, supplied by Dr. Hall, was freed of phenothiazine stabilizer and dimethylformamide by dissolving in diethyl ether, washing with water, drying for several hours over neutral alumina, and vacuum distilling twice from molecular sieves. It was then stored under nitrogen in a Dry Ice box. Methyl 1-bicyclobutanecarboxylate was prepared by the procedure of Hall et al. (1971b) and stored under nitrogen in a Dry Ice box. Styrene (Matheson, Coleman and Bell) was freed of inhibitor by vacuum distillation and stored under nitrogen in a Dry Ice box. Acrylonitrile (Matheson, Coleman and Bell) was likewise freed of inhibitor by vacuum distillation from phosphorus pentoxide and stored under nitrogen in a refrigerator. Tetramethylenesulfone (Aldrich) was distilled from phosphorus pentoxide to remove water. Zinc chloride (Matheson, Coleman and Bell), benzoyl peroxide (Matheson, Coleman and Bell), azobisisobutyronitrile (Dupont), and all other chemicals were used without further purification.

Nuclear magnetic resonance (nmr) spectra were determined on either a Varian model A-60 spectrometer at 60 MHz or a Varian model HA-100 spectrometer at

100 MHz using tetramethylsilane as an internal or external standard. Infrared (ir) spectra were obtained with a Perkin-Elmer 337 grating infrared spectrophotometer. A polystyrene film was used to calibrate the instrument. Vapor phase chromatography (vpc) was carried out on a Varian Aerograph series 1700 with a 5 foot 3% SE-30 Verapore 30/120 mesh column and a Leeds and Northrup speedomax H recorder. All polymers subjected to elemental analysis were dried in an Abderhalden drying pistol with boiling xylene. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tennessee. Calculated values are based on 1:1 composition. In all cases, a small amount of zinc chloride was held by the polymer despite several reprecipitations. Therefore, adjusted values are without zinc chloride. Inherent viscosities were determined with an Ostwald-Fenske viscometer at 30°. The concentration of all solutions was 0.1 g per dl in dimethylformamide.

Copolymerization of Acrylonitrile and Styrene in Bulk

The procedure of Yabumoto et al. (1969) was used. A test tube was flushed with nitrogen and charged with 1.2 g (12 mmol) of zinc chloride, 0.58 ml (12 mmol) of acrylonitrile and 1.0 ml (12 mmol) of styrene. The

solution was stirred and heated to 60°. A solid plug readily formed. The plug was dissolved in acetone and precipitated in methanol. An infrared spectrum of a polymer film showed that the polymer contained both acrylonitrile and styrene. An nmr spectrum of the polymer in deuterated acetone indicated, by comparison of the integration of aromatic and aliphatic protons, that there was more acrylonitrlie than styrene in the polymer.

Copolymerization of 1-Bicyclobutanecarbonitrile and Styrene in Bulk

1-Bicyclobutanecarbonitrile (0.5 ml, 5.6 mmol) and 0.67 ml (5.6 mmol) of styrene were mixed in a test tube under nitrogen at -30°. The mixture was allowed to warm until the styrene just melted. Then 0.8 g (5.6 mmol) of zinc chloride and a few mg of benzoyl peroxide were added. The mixture was allowed to warm slowly to room temperature. After a few hours, the mixture was hard. The test tube was broken and the hard plug ground up. The particles were stirred in diethyl ether for several hours to remove any zinc chloride and the ether was then added to methanol, but no precipitate formed. The polymer swelled in dimethylformamide but only a small fraction would dissolve. The remaining gel was washed with methanol and filtered.

An infrared spectrum of the polymer in a KBr pellet showed the presesence of both 1-bicyclobutanecarbonitrile and styrene. The following solvents were tried on the polymer at room temperature: Dimethylformamide, chloroform, acetone, dimethylsulfoxide, water, carbon tetrachloride, hexafluoroisopropanol, diethyl ether, benzene, hexamethylphosphoramide, tetramethylenesulfone, N-methylpyrrolidone and sulfuric acid. The following solvents were tried at their boiling points or at 160°: N-methylpyrrolidone, chloroform, acetone, hexamethylphosphoramide, methanesulfonic acid, and hexafluoroiospropanol. In none of these solvents was the polymer soluble. It was also found to be insoluble in N-methylpyrrolidone in the presence of sodium methoxide and methanol.

Anal. Calcd. for $C_{13}H_{13}N$: C, 85.20; H, 7.17; N, 7.64.
Found: C, 85.46; H, 7.27; N, 7.15.

Copolymerization of 1-Bicyclobutanecarbonitrile and Vinyl Butyl Ether in Bulk

A Catalytic Amount of Zinc Chloride. 1-Bicyclobutanecarbonitrile (0.5 ml, 5.6 mmol), 0.74 ml (5.6 mmol) of vinyl butyl ether, and a catalytic amount of zinc chloride were placed in a test tube under nitrogen. The test tube was stoppered and placed in a refrigerator. After several days, only a small amount of polymer had formed. The test tube was warmed to room temperature.

After four days, there was still little polymer. Vapor phase chromatography of the liquid showed the presence of only starting materials. The small amount of polymer which had formed was insoluble in N-methylpyrrolidone.

An Equivalent of Zinc Chloride. 1-Bicyclobutanecarbonitrile (0.5 ml, 5.6 mmol), 0.74 ml (5.6 mmol) of vinyl butyl ether, and 0.8 g (5.6 mmol) of zinc chloride were mixed in a test tube under nitrogen. The test tube was stoppered, and placed in a refrigerator. It polymerized rapidly. The polymer was ground up and soaked in tetrahydrofuran for three days to remove the zinc chloride. The tetrahydrofuran mixture was filtered and the polymer placed in N-methylpyrrolidone. When sodium methoxide in methanol was added, the polymer turned brown and dissolved. It was precipitated in methanol. An infrared spectrum of the polymer in a KBr pellet and an nmr spectrum, run in deuterated dimethylsulfoxide, showed that vinyl butyl ether had been incorporated into the polymer.

Copolymerization of Methyl 1-Bicyclobutanecarboxylate and Styrene in Bulk

A Catalytic Amount of Zinc Chloride. Methyl 1-bicyclobutanecarboxylate (0.45 g, 4.0 mmol), 0.46 ml (4.0 mmol) of styrene,, and a catalytic amount of zinc chloride were placed in a test tube under nitrogen.

The test tube was stoppered and placed in a refrigerator for two days. At the end of this time, since no polymer had formed, more zinc chloride was added and the test tube allowed to warm to room temperature. After two weeks, the liquid was very viscous. It was dissolved in chloroform and the polymer precipitated in methanol. An infrared spectrum of a polymer film showed the presence of both methyl 1-bicyclobutanecarboxylate and styrene in the polymer.

An Equivalent of Zinc Chloride. Methyl 1-bicyclobutanecarboxylate (0.45 g, 4.0 mmol), 0.46 ml (4.0 mmol) of styrene and 0.55 g (4.0 mmol) of zinc chloride were mixed in a test tube under nitrogen. The test tube was stoppered and placed in a refrigerator for three days. It polymerized to a solid plug which was partially soluble in dimethylformamide. The plug was dissolved and precipitated in methanol.

Homopolymerization of 1-Bicyclobutanecarbonitrile in Bulk

A Catalytic Amount of Zinc Chloride. 1-Bicyclobutanecarbonitrile (0.5 ml, 5.6 mmol) and a catalytic amount of zinc chloride were placed in a test tube under nitrogen. The test tube was stoppered and placed in a refrigerator. After four days, the liquid in the tube was hard. The test tube was broken and the polymer

ground up and washed with diethyl ether to remove the zinc chloride. The following solvents were tried cold and hot: dimethylsulfoxide, N-methylpyrrolidone, dimethylformamide, and hexafluoroisopropanol. In all cases, a small amount dissolved, but most of the polymer only swelled. That which did dissolve was precipitated in methanol and an infrared spectrum taken in a KBr pellet. The spectrum showed CN at 2240 cm^{-1} and C=C=N- at 2000 cm^{-1}. The polymer was soluble in N-methylpyrrolidone after sodium methoxide in methanol was added. However, when the solvent was poured into methanol, no precipitate formed. Evaporation of the methanol and N-methylpyrrolidone followed by washing with water to remove the sodium methoxide gave only a little residue. An infrared spectrum of the residue showed the presence of poly(1-bicyclobutanecarbonitrile), but most of the polymer must have been destroyed by the base.

An Equivalent of Zinc Chloride. 1-Bicyclobutanecarbonitrile (0.5 ml, 5.6 mmol) and 0.8 g (5.6 mmol) of zinc chloride were placed in a test tube under nitrogen. The test tube was stoppered and placed in a refrigerator. Polymer formed rapidly. The polymer was ground up and soaked three days in tetrahydrofuran to remove the zinc chloride. The polymer did not dissolve in N-methylpyrrolidone to any appreciable degree, even

after sodium methoxide in methanol had been added. The mixture was filtered, and what little polymer had dissolved was precipitated in methanol. An infrared spectrum of this polymer in a KBr pellet showed poly (1-bicyclobutanecarbonitrile).

Homopolymerization of Methyl 1-Bicyclobutanecarboxylate in Bulk

A Catalytic Amount of Zinc Chloride. Methyl 1-bicyclobutanecarboxylate (0.45 g, 4.0 mmol) was placed in a test tube with a catalytic amount of zinc chloride under nitrogen. The test tube was stoppered and left for three days in a refrigerator. It polymerized to a very viscous liquid. The polymer was dissolved in dimethylformamide and poured into methanol. Some of the polymer remained insoluble and a substantial amount seemed to have been lost in the precipitation process, for when the methanol was evaporated, only a small residue remained.

An Equivalent of Zinc Chloride. Methyl 1-bicyclobutanecarboxylate (0.45 g, 4.0 mmol) and 0.55 g (4.0 mmol) of zinc chloride were placed in a test tube under nitrogen. The test tube was stoppered and placed in a refrigerator for three days. It polymerized, but most of the polymer was insoluble in dimethylformamide.

Homopolymerization of Methyl 1-Bicyclobutanecarboxylate in Tetramethylenesulfone

A Catalytic Amount of Zinc Chloride. Methyl 1-bicyclobutanecarboxylate (0.4 ml, 4.0 mmol) and a catalytic amount of zinc chloride were mixed with several ml of tetramethylenesulfone in a test tube under nitrogen. After three days at room temperature, a viscous liquid had formed. It was dissolved in chloroform and precipitated in methanol. The polymer was redissolved in chloroform, precipitated in methanol, and dried; yield, 0.3 g (62%). An infrared spectrum of a polymer film showed it to be poly(methyl 1-bicyclobutanecarboxylate); η_{inh}, 5.13.

Anal. Calcd. for $C_6H_8O_2$: C, 64.27; H, 7.19; O, 28.54.

Found: C, 63.96; H, 7.09; O, 27.48; Cl, 1.86.

Adjusted: C, 64.91; H, 7.20; O, 27.89.

An Equivalent of Zinc Chloride. Methyl 1-bicyclobutanecarboxylate (0.4 ml, 4.0 mmol) and 0.55 g (4.0 mmol) of zinc chloride were mixed with several ml of tetramethylenesulfone in a test tube under nitrogen. After three days at room temperature, a rubbery plug had formed. The plug was dissolved in dimethylformamide and precipitated in methanol. The polymer was redissolved in dimethylformamide, precipitated in methanol, and dried; yield, 0.2 g (45%). An infrared spectrum of a polymer film showed it to be poly(methyl 1-bicyclobutanecarboxylate); η_{inh}, 4.64.

Anal. Calcd. for $C_6H_8O_2$: C, 64.27; H, 7.19; O, 28.54.
Found: C, 64.59; H, 7.03; O, 28.30; Cl, 0.08.
Adjusted: C, 64.64; H, 7.04; O, 28.32.

Copolymerization of Methyl 1-Bicyclobutanecarboxylate and Styrene in Tetramethylenesulfone

A Catalytic Amount of Zinc Chloride. Methyl 1-bicyclobutanecarboxylate (0.4 ml, 4.0 mmol), 0.46 ml (4.0 mmol) of styrene, and a catalytic amount of zinc chloride were mixed with several ml of tetramethylene-sulfone in a small flask under nitrogen. The mixture was stirred at room temperature for three days. The solution had not become very viscous, so a small amount of benzoyl peroxide was added, and the solution heated to 60°. After three days, the solution was very viscous. It was poured into methanol, and the polymer filtered and dried. The polymer was very powdery, indicating low molecular weight; yield, 0.5 g (55%). An infrared spectrum of a polymer film and an nmr spectrum, run in deuterated chloroform, showed both monomers to be present in the polymer.

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46; O, 14.79.
Found: C, 79.02; H, 7.13; O, -----; Cl, 1.74.
Adjusted: C, 81.87; H, 7.39; O, 10.74.

An Equivalent of Zinc Chloride. Methyl 1-bicyclobutanecarboxylate (0.4 ml, 4.0 mmol), 0.46 ml

(4.0 mmol) of styrene and 0.55 g (4.0 mmol) of zinc chloride were mixed with several ml of tetramethylene-sulfone in a small flask under nitrogen. The solution was stirred at room temperature for three days. The solution had not become very viscous, but was poured into methanol anyway. The polymer was filtered off. It was very powdery, indicating low molecular weight; yield, 0.1 g (11%). An infrared spectrum of a polymer film and an nmr spectrum, run in deuterated chloroform, showed both monomers to be present in the polymer.

The above polymerization was repeated with a few mg of benzoyl peroxide added. After two days, the solution was not very viscous, so a few more mg of benzoyl peroxide were added and the solution heated to 60°. After four days, the solution was still not very viscous, but was poured into methanol anyway. The polymer was filtered off, dried, dissolved in dimethyl-formamide, reprecipitated in methanol, filtered, and dried again; yield, 0.4 g (44%). An infrared spectrum of a polymer film showed both monomers to be present in the polymer; η_{inh}, 0.39.

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46; O, 14.79.

Found: C, 76.20; H, 7.38; O, 12.40; Cl, 0.35.

Adjusted: C, 79.39; H, 7.69; O, 12.92.

Homopolymerization of 1-Bicyclobutanecarbonitrile in Tetramethylenesulfone

A Catalytic Amount of Zinc Chloride. 1-Bicyclobutanecarbonitrile (0.5 ml, 5.7 mmol) and a catalytic amount of zinc chloride were mixed with several ml of tetramethylenesulfone in a small flask under nitrogen. The solution was stirred at room temperature for two days. After this period of time, the solution was very viscous. It was poured into methanol and the polymer was blended, filtered, dried, dissolved in dimethylformamide, reprecipitated in methanol, and dried again; yield, 0.15 g (33%). An infrared spectrum of a polymer film showed it to be poly(1-bicyclobutanecarbonitrile); η_{inh}, 5.77.

Anal. Calcd. for C_5H_5N: C, 75.92; H, 6.37; N, 17.71.
Found: C, 72.54; H, 6.11; N, 17.59; Cl, <0.1.
Adjusted: C, 75.37; H, 6.35; N, 18.28.

An Equivalent of Zinc Chloride. 1-Bicyclobutanecarbonitrile (0.5 ml, 5.7 mmol) and 0.78 g (5.7 mmol) of zinc chloride were mixed with several ml of tetramethylenesulfone in a small flask under nitrogen. The solution was stirred at room temperature for one day. After this period of time, the solution was hard. It was dissolved in dimethylformamide and precipitated in methanol. The polymer was blended, filtered, dried, redissolved in dimethylformamide, precipitated in

methanol and dried again; yield, 0.4 g (88%). An infrared spectrum of a polymer film showed it to be poly (1-bicyclobutanecarbonitrile); η_{inh}, 5.82.

Anal. Calcd. for C_5H_5N: C, 75.92; H, 6.37; N, 17.71.
Found: C, 74.04; H, 6.26; N, 18.05; Cl, <0.1.
Adjusted: C, 75.28; H, 6.37; N, 18.35.

Copolymerization of 1-Bicyclobutanecarbonitrile and Styrene in Tetramethylenesulfone

A Catalytic Amount of Zinc Chloride. 1-Bicyclobutanecarbonitrile (0.5 ml, 5.7 mmol), 0.66 ml (5.7 mmol) of styrene and a catalytic amount of zinc chloride were mixed with several ml of tetramethylenesulfone in a small flask under nitrogen. The solution was stirred at room temperature for four days. After this period of time, no polymer had formed, so the solution was heated to 60°. After two days, still no polymer had formed, so a little benzoyl peroxide was added. After one week, the solution was fairly viscous. It was dissolved in dimethylformamide and poured into methanol. The polymer was filtered, dried, redissolved in dimethylformamide, precipitated in methanol and dried again; yield, 0.9 g (90%). An infrared spectrum of a polymer film showed both monomers to be present; η_{inh}, 0.95.

Anal. Calcd. for $C_{13}H_{13}N$: C, 85.20; H, 7.15; N, 7.64.
Found: C, 84.25; H, 7.00; N, 6.49; Cl, 0.68.
Adjusted: C, 86.20; H, 7.16; N, 6.64.

An Equivalent of Zinc Chloride. 1-Bicyclobutanecarbonitrile (0.5 ml, 5.7 mmol), 0.66 ml (5.7 mmol) of styrene, and 0.78 g (5.7 mmol) of zinc chloride were mixed with several ml of tetramethylenesulfone in a small flask under nitrogen. The solution was stirred at room temperature for four days. After this period of time, the solution was very viscous. It was dissolved in dimethylformamide and poured into methanol. The polymer was filtered, dried, redissolved in dimethylformamide, precipitated in methanol, filtered and dried again; yield, 0.6 g (63%). An infrared spectrum of a polymer film showed both monomers to be present in the polymer; η_{inh}, 2.23.

Anal. Calcd. for $C_{13}H_{13}N$: C, 85.20; H, 7.15; N, 7.64.
Found: C, 85.02; H, 6.98; N, 7.71; Cl, 0.28.
Adjusted: C, 85.27; H, 7.00; N, 7.73.

Homopolymerization of 1-Bicyclobutanecarbonitrile in the Presence of a Chain-Transfer Agent

1,3-Dimethoxybenzene. 1-Bicyclobutanecarbonitrile (0.5 ml, 5.7 mmol) and 0.05 ml (10%) of 1,3-dimethoxybenzene were mixed with several ml of tetramethylenesulfone in a small flask under nitrogen. To this solution was added 0.78 g (5.7 mmol) of zinc chloride. The solution was stirred at room temperature for two days. The resulting polymer was dissolved in dimethylformamide,

precipitated in methanol, blended, filtered, dried, redissolved in dimethylformamide, precipitated in methanol, blended, filtered, and dried again; yield, 0.5 g (100%); η_{inh}, 4.88.

Anal. Calcd. for C_5H_5N: C, 75.92; H, 6.37; N, 17.71.

Found: C, 72.91; H, 6.26; N, 17.28; Cl, 0.19.

Adjusted: C, 75.59; H, 6.49; N, 17.92.

Carbon Tetrachloride. The above procedure was repeated using 0.05 ml (10%) of carbon tetrachloride in place of the 1,3-dimethoxybenzene; yield, 0.5 g (100%); η_{inh}, 6.68.

Anal. Calcd. for C_5H_5N: C, 75.92; H, 6.37; N, 17.71.

Found: C, 74.19; H, 6.25; N, 17.28; Cl, 0.25.

Adjusted: C, 75.92; H, 6.40; N, 17.68.

Copolymerization of 1-Bicyclobutanecarbonitrile and Styrene in the Presence of a Chain-Transfer Agent

1,3-Dimethoxybenzene. 1-Bicyclobutanecarbonitrile (0.5 ml, 5.7 mmol), 0.66 ml (5.7 mmol) of styrene, and 0.1 ml (10%) of 1,3-dimethoxybenzene were mixed with several ml of tetramethylenesulfone in a small flask under nitrogen. To this solution was added 0.78 g (5.7 mmol) of zinc chloride. The solution was stirred at room temperature for two days. The resulting polymer was dissolved in dimethylformamide, precipitated in methanol, blended, filtered, dried, redissolved in

dimethylformamide, precipitated in methanol, and dried again; yield, 0.4 g (38%); η_{inh}, 2.31.

Anal. Calcd. for $C_{13}H_{13}N$: C, 85.20; H, 7.15; N, 7.64.
Found: C, 85.18; H, 7.15; N, 7.43; Cl, ----.
Adjusted: C, 85.38; H, 7.17; N, 7.45.

Carbon Tetrachloride. The above procedure was repeated using 0.1 ml (10%) of carbon tetrachloride in place of the 1,3-dimethoxybenzene; yield, 0.4 g (38%); η_{inh}, 2.47.

Anal. Calcd. for $C_{13}H_{13}N$: C, 85.20; H, 7.15; N, 7.64.
Found: C, 83.46; H, 7.02; N, 7.43; Cl, 0.49.
Adjusted: C, 85.24; H, 7.17; N, 7.59.

Copolymerization of 1-Bicyclobutanecarbonitrile and Styrene at Different Monomer Feed Ratios

1:3:1. 1-Bicyclobutanecarbonitrile (0.25 ml, 2.9 mmol), 0.99 ml (8.5 mmol) of styrene, and 0.39 g (2.9 mmol) of zinc chloride were mixed with tetramethylene-sulfone in a small flask under nitrogen. The solution was stirred at room temperature for 24 hours. The polymer was precipitated in methanol, filtered, and dried; yield, <0.05 g ($<10\%$, based on a 1:1 copolymer).

Anal. Calcd. for $C_{13}H_{13}N$: C, 85.20; H, 7.15; N, 7.64.
Found: C, 80.49; H, 6.85; N, 3.77; Cl, 2.54.
Adjusted: C, 88.34; H, 7.52; N, 4.14.

This corresponds to 27.4% 1-bicyclobutanecarbonitrile in the copolymer.

3:1:3. 1-Bicyclobutanecarbonitrile (0.75 ml, 8.5 mmol), 0.33 ml (2.9 mmol) of styrene, and 1.16 g (8.5 mmol) of zinc chloride were mixed with several ml of tetramethylenesulfone in a small flask under nitrogen. The solution was stirred at room temperature for 2.5 hours. The polymer was precipitated in methanol, blended, filtered, dissolved in dimethylformamide, reprecipitated in methanol, blended, filtered, and dried. The polymer was then extracted in a soxhlet with methanol for two days and dried again; yield, 0.45 g (85%, based on a 1:1 copolymer); η_{inh}, 2.85.

Anal. Calcd. for $C_{13}H_{13}N$: C, 85.20; H, 7.15; N, 7.64.

Found: Zn, 11.06; C, 82.87; H, 6.86; N, 8.00; Cl, 1.17.

Adjusted: C, 84.79; H, 7.02; N, 8.19.

This corresponds to 53.7% 1-bicyclobutanecarbonitrile in the copolymer.

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