

Polymerization of Tetrahydrofuran

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I. INTRODUCTION

In studying the utility of boron trifluoride (BF_3) solutions as curing agents for epoxy resins, it was observed that a 10% solution of BF_3 in tetrahydrofuran (THF) polymerized after standing overnight at room temperature. A literature search revealed that THF had previously been polymerized by BF_3 only in conjunction with other initiators. Engelhardt¹ used 0.4 to 2 wt.-% BF_3 with ethyl diazoacetate or diazomethane to obtain THF polymers having molecular weights of 500-5000. When the diazo compound was omitted, however, no polymer was produced. Murbach and Adicoff,² in synthesizing copolymers of ethylene oxide and THF, reported that no homopolymerization of THF occurred under the conditions used (1 to 6 mole-% BF_3 at 0°). In his review of the polymerization of cyclic ethers, Eastham³ stated that Meerwein had obtained THF polymers with maximum molecular weight of about 8000 by using tertiary alkyl oxonium salts formed by the interaction of BF_3 -diethyl etherate with ethylene oxide or its derivatives. Eastham observed also that antimony pentachloride was the only Friedel-Crafts catalyst studied by Meerwein that was sufficiently active to initiate the polymerization of THF without cocatalysts. Recently, Muetterties⁴ patented the use of phosphorus pentafluoride without co-reactants as an initiator for the polymerization of THF.

Meerwein⁵ depicted the polymerization as being initiated by some cation and propagated by a carbonium ion mechanism. The reaction reaches an equilibrium between monomer and polymer and finally terminates when the oxonium ion at the end of the polymer chain reacts with impurities or with the precipitating solvent during purification.

This paper deals with polymerization of THF in which BF_3 is the sole initiator. The essential difference between this and previous work is that here BF_3 is used at relatively high concentrations.

This report also describes some of the properties of the very high molecular weight THF polymer obtained from the reaction described.

II. EXPERIMENTAL PROCEDURE

Bulk polymerizations of THF were effected by allowing solutions of BF_3 in THF to stand in closed vials at the desired conditions. These solutions were made up to the required weight per cent concentrations by diluting the BF_3 -THF coordination complex with THF. The complex was prepared by passing cylinder BF_3 directly into THF until the weight increase corresponded to the absorption of one mole of BF_3 . The temperature of this reaction was maintained below 45°C. by cooling with an ice bath as necessary. At the beginning of the work commercial THF was vacuum distilled over sodium hydroxide and stored in dark bottles until used. Later, however, these precautions were found to be unnecessary for our purposes since very similar products resulted when the reagent grade THF was used directly. Extreme precautions to exclude moisture were not observed.

The polymer was purified by repeatedly dissolving it in THF and precipitating it from water until the flame test for boron was negative. In most cases two such operations were sufficient. The polymer was then dried several days under vacuum at room temperature.

Intrinsic viscosities were determined in THF at 25°C. Use of the monomer as the solvent was shown not to be a complicating feature since intrinsic viscosities determined in methylene chloride corroborated the THF values in twenty check tests.

Ultraviolet radiation was conducted under ASTM Method D620-57T. Elemental, infrared, and x-ray diffraction analyses were made by the Analytical Department and intrinsic viscosities and mechanical properties were determined by the Physical Testing Department at Air Reduction Central

Research Laboratories. Crystalline melting points as determined on a Fisher-Johns Melting Point Apparatus are uncorrected.

III. RESULTS AND DISCUSSION

A. Polymerization Variables

1. Preliminary Results

Before making a study of the polymerization variables, the general appearance of various solutions of BF_3 in THF after standing was noted as shown in Table I. These preliminary results

TABLE I
Appearance of THF Solutions of BF_3

| BF_3 concn., % | After 3 days at 5°C. | After subsequent reaction at 25°C. |
|-------------------------------|---|---|
| 1 | Clear, colorless, fluid soln. | Clear, colorless, fluid soln. after several months |
| 3 | " | Clear, colorless, slightly viscous soln. after several months |
| 5 | Clear, colorless, viscous soln. | Clear, colorless, weak gel after 1 week |
| 9 | Clear, colorless gel | Slightly dark, firm gel after 1 week |
| 17 | Gray, opaque solid | Dark, opaque solid after 1 week |
| 28 | Gray, opaque solid, floating on very dark, fluid soln. | Very dark solid and soln. after several days |
| 48 | Clear, slightly dark, fluid soln. | Clear, slightly dark, fluid soln. after several days; very dark, fluid soln. after 1 week |

indicate that at 3% BF_3 the polymerization does not proceed at a useful rate and that at a BF_3 concentration as high as 28%, deterioration is extensive. Both the polymerization and the degradation reactions are seen to proceed more rapidly at the higher BF_3 concentrations and at the higher temperatures.

This information led to the primary investigation which was concerned with the effect of BF_3 concentration, reaction temperature, and reaction time on molecular weight and conversion of the polymer. The crystalline melting point of the polymer was also originally considered to be dependent on these factors. It became apparent as the work progressed, however, that the melting points of all of these products were essentially constant. The degrees of polymerization are such that all the points lie on the plateau of the classical molecular weight versus melting point curve.⁶

2. Effect of BF_3 Concentration and Polymerization Temperature

In this experiment THF was polymerized for nine days at -50 , -5 , 10 , and 25°C . with 5, 10, 15, and 20% BF_3 . As might be expected from the diverse conditions employed, the behavior of these solutions varied considerably. At the three higher temperatures, 25 , 10 , and -5°C ., the polymeric products were soluble in the excess monomer. These solutions accordingly grew more and more viscous as the reaction proceeded and eventually gelled in those cases for which the conversion was above 25%. The conditions of -50°C . and 5% BF_3 were so mild that no polymer could be isolated; only a colloidal solution resulted when this reaction product was poured into water. At the three higher initiator concentrations at -50°C ., essentially the entire yield was provided by white, fluffy solids which precipitated during the reaction.

The effect of BF_3 concentration and temperature on intrinsic viscosity is shown in Figure 1. In general, higher molecular weights were reached at the lower initiator concentrations. For each initiator concentration the intrinsic viscosity assumed a maximum at -5°C ., intermediate values at -50 and 10°C ., and a minimum at 25°C . The values at -50°C . break the trend of increasing intrinsic viscosities with decreasing temperatures. Since -50°C . is the temperature at which the product precipitated during the reaction, it may be that the polymer became insoluble in the monomer before the equilibrium chain length could be attained. This explanation suggests that the highest molecular weight may be reached at the lowest temperature that does not precipitate the polymer.

The variation of per cent conversion with initiator concentration and temperature is shown in Figure 2. If the data at -50°C . are disregarded, and this may reasonably be done since they were obtained under precipitating conditions, the changes due to temperature seem to be reasonably consistent. As the temperature increased conversion increased continuously at 5% BF_3 , changed little at 15%, and decreased continuously at 20%. At the two lower temperatures, -50 and -5°C ., the conversion varied directly with the initiator concentration. Except for the low value of 20% BF_3 , this is also true at 25°C . The polymer obtained under these relatively vigorous conditions, 20% BF_3 and 25°C ., seemed to possess a basically different structure from the others in the study.

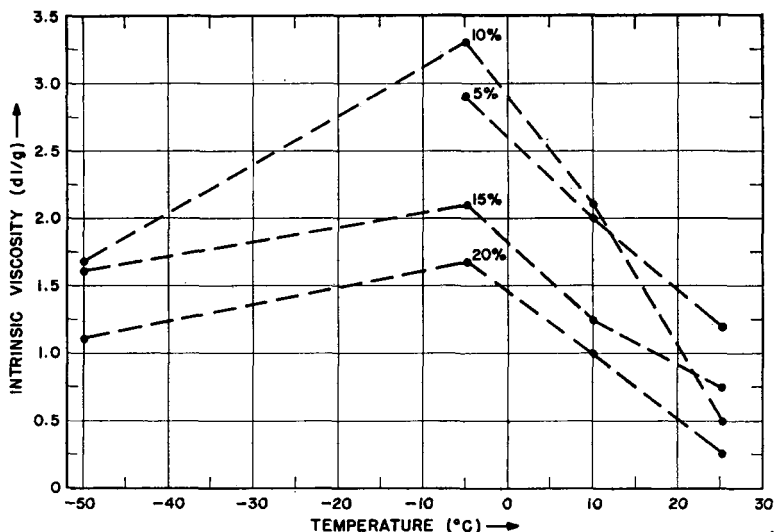


Fig. 1. Effect of BF_3 concentration and polymerization temperature on intrinsic viscosity.

The intrinsic viscosity slope constant (k') for this product was 1.36, quite different from the average value of 0.48 for all the polymers. This result suggests that the high catalyst concentration and high temperature produced an extensively branched polymer compared to the more linear structure afforded under milder conditions.

The values for 10% BF_3 are anomalous on both the conversion and intrinsic curves since they cut across other constant-concentration lines. Although 10% BF_3 is an intermediate initiator concentration, its use resulted in the highest intrinsic viscosity and in the highest conversion obtained in the study.

3. Effect of Polymerization Time

A large amount of a 15% solution of BF_3 in THF was divided into twenty portions of 20.0 g. each and allowed to react at -5°C . One portion was removed daily and diluted or dissolved in a specific amount of THF. The Brookfield viscosity of this solution was measured and after the polymer was precipitated and dried, the conversion and intrinsic viscosity were recorded. The solutions were converted to clear gels after three days and to opaque, silver solids after nine days. Dissolution of the samples became progressively more difficult after they gelled.

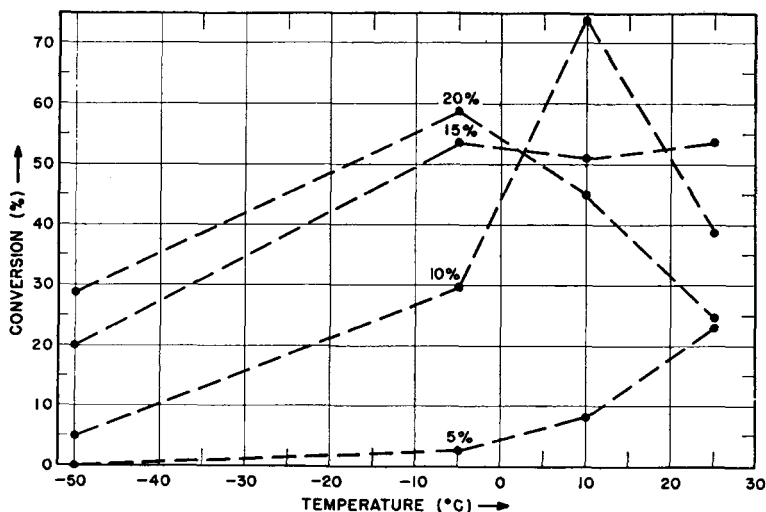


Fig. 2. Effect of BF_3 concentration and polymerization temperature on conversion.

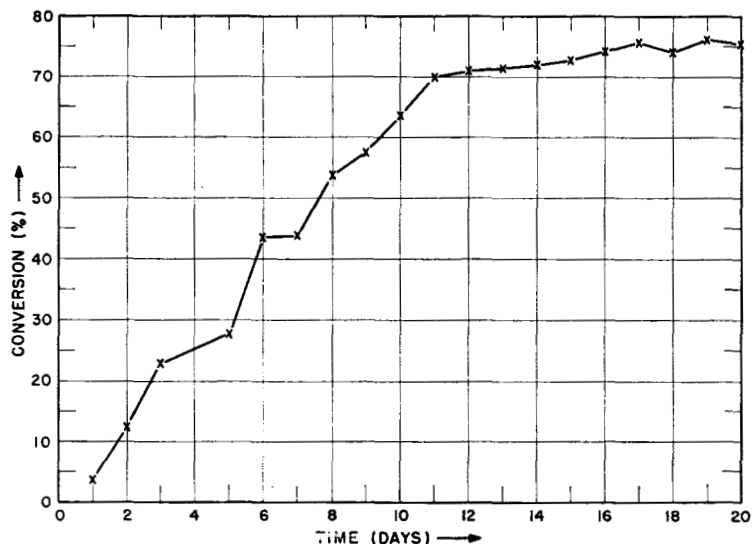


Fig. 3. Effect of polymerization time on conversion.

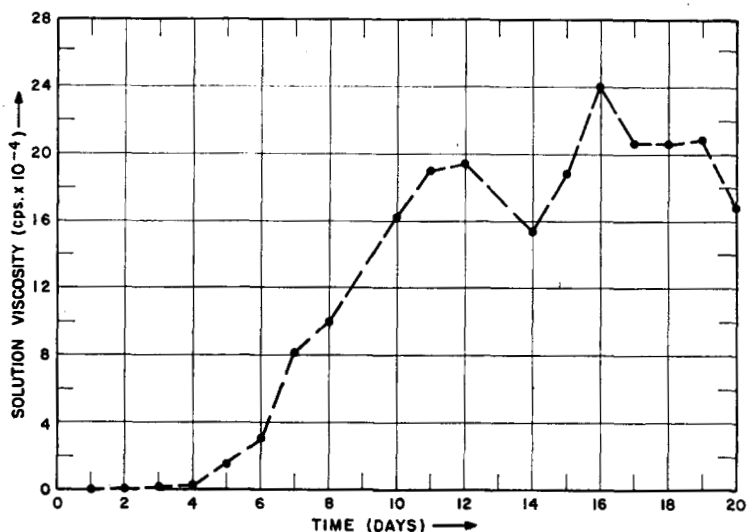


Fig. 4. Effect of polymerization time on viscosity of reaction mixture.

The intrinsic viscosity, after rising to 1.6 after one day, fluctuated randomly about an average of 2.6 for the duration of the testing period. If this polymerization is an equilibrium reaction, the equilibrium molecular weight is apparently reached in about two days.

The relationship between conversion and polymerization time is shown in Figure 3. This graph seems to consist of two distinct sections. In the first the conversion increased from 3.5% after one day to 70.1% after eleven days. The straight line through these points passes very near the origin and has a slope of about 6.5% per day. The section

after eleven days is also approximately linear but it has a very small slope, since the maximum difference in conversions over this period was only 5%. Gelation and solidification of the samples apparently did not affect the rate of conversion because the curve does not change particularly at three or nine days.

Although the viscosity of the reaction mixture is merely the result of the effects of molecular weight and conversion, it is important in the practical manipulation of the product. The graph of Brookfield viscosity versus polymerization time is given in Figure 4. Here again two sections are

apparent. Over the first eleven days the curve is nearly parabolic. This corresponds to the steep linear portion on the conversion-time graph (Fig. 3) and is the relationship to be expected if molecular weight were not a variable. Over the last nine days, while the conversion increased very little, the viscosity of the reaction mixture underwent large fluctuations about a constant value. These fluctuations may have been due to the increased importance of dissolution technique and the reduced instrument reliability at the very high viscosities.

4. Miscellaneous Results

Because the bulk polymerization of THF frequently resulted in gelled products which were difficultly soluble, even in the most efficient solvents, solution polymerizations were investigated briefly. Table II summarizes the conditions and results of these experiments. No conditions were found which gave polymers comparable to those obtained from bulk polymerizations.

TABLE II
Solution Polymerization of THF by BF_3

| Solvent | THF/ solvent/ BF_3 ratio | Temp., °C. | Time | Results |
|-----------------|---|---------------|------------|---|
| Methanol | 1/1/0.08 | -5 | 7 days | No isolable product |
| " | 1/1/0.15 | -5 | " | " |
| Benzene | 1/1/0.08 | -5 | " | " |
| " | 1/1/0.15 | -5 | " | Conversion = 11%; $[\eta]$ = 1.5; $k' = 0.37$ |
| Hexane | 1/1/0.12 | -5 and 20 | 1 mo. " | Conversion = 5%; $[\eta]$ = 1.4; $k' = 0.53$ |
| Chloro- form | 1/1/0.10 | -5 and 20 | " " | Tacky semisolid |

One of the chief deficiencies of the bulk polymerization of THF by BF_3 is the long reaction time required for high conversions of good products. It was found that the time to gelation could be considerably reduced by incorporating small amounts of cyclic ethers with strained rings. When 3,3-bis(chloromethyl)oxacyclobutane and phenyl glycidyl ether were used as coinitiators, the polymerization rate increased so that in some cases waxy solids were obtained after only a few hours. After purification, however, the products proved to be tacky semisolids and were not investigated further at that time.

The use of diepoxides was somewhat more successful. For example, after one hour a 10% solution of BF_3 in THF with less than 0.5% of a low molecular weight epoxy resin gave a solid product with a crystalline melting point of 43°C., an intrinsic viscosity of 1.2, and a slope constant of 0.49. The value for the slope constant is essentially the same as those from the unaccelerated reactions, thus suggesting that the polymers have similar structures. A major problem with the use of the diepoxides was the ease with which a crosslinked product formed. These rubbery masses were very strong, but the occluded initiator promoted degradation after several days.

BF_3 as the diethyl etherate is also an effective catalyst. At 10% BF_3 and -5°C. a polymer was obtained after ten days which was practically identical with that produced by the THF complex under similar conditions.

B. Properties of the THF Polymer

1. Types and General Appearance

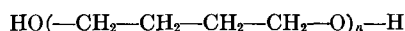
This investigation and the available literature indicate the existence of two different types of THF polymers. The first, which we will call Type I, is the product obtained when relatively high concentrations of BF_3 are used; it is the primary concern of this report. The Type I polymer is precipitated from water as a flexible, strongly cohesive, nontacky, white solid. When fused at a temperature slightly above its crystalline melting point, it becomes soft but remains in a nontacky, nonfluid, rubbery condition. After having recrystallized, it is a tan, leathery material which can be cold-drawn into a strong fiber or anisotropic film. The only previous description of a THF polymer with similar characteristics concerns the use of phosphorus pentafluoride as the initiator.⁴

The Type II polymer has been the subject of many investigations; it is the one afforded by low concentrations of BF_3 with co-initiators and by most other cationic initiators. It was encountered incidentally in this work as the product from solution polymerizations, from most accelerated reactions, and from reactions carried out under relatively vigorous conditions, 20% BF_3 and 25°C., for example. These THF polymers are tan, soft, and very tacky when first precipitated even from such a nonsolvent as water. Crystallization takes place relatively slowly so that specimens flow considerably before they solidify.

The crystalline modifications of Types I and II appear to be similar except that the latter are somewhat weaker and more friable. The two types have approximately the same crystalline melting point.

2. Structure

Previous work⁵ concerning the mechanism of THF polymerization suggests the following structure for the polymer purified with water:



The calculated values for the segment are C = 66.7%, H = 11.1%, and O = 22.2%. Elemental analysis performed on the THF polymer prepared here gave the composition as C = 68.2%, H = 9.2%, and O = 22.2%. Although the analysis is high for carbon and low for hydrogen, the simplest rational empirical formula is C₄H₈O. The fact that the total of the experimental values is 99.6% lends support to this formula. No boron was detected by emission spectrographic analysis of the polymer despite the high concentration of BF₃ in the reaction.

An approximate value of the degree of polymerization represented in the above structure was obtained from the intrinsic viscosity using a modified Staudinger equation, $[\eta] = KM^a$. If 10^{-4} and 0.8 are used for the constants, K and a , respectively, a molecular weight of about 400,000 and a degree of polymerization of about 5500 is calculated for a product with an intrinsic viscosity of 3.0. This is probably a conservative estimate since it is doubtful that the polymer chains are as stiff as the proposed value of a indicates. However, this molecular weight is similar to the one determined osmotically for the polymer initiated by PF₅. The Fikentscher K -value⁷ corresponding to this molecular weight is about 125; Meerwein has reported K -values of less than 100 for THF polymers produced with cocatalysts. Considering these large molecular weights, it is not surprising that infrared analysis of the polymer failed to detect any evidence of the hydroxyl endgroups indicated in the structure.

The slope of the least-squares line fitted to a plot of slope constant versus per cent conversion for twenty-eight Type I products is negligible (-0.0016). The degree of branching and cross-linking in the polymer is therefore probably very slight because the slope constant is essentially independent of the amount of polymer produced. This result substantiates the inference of linearity

which was made from cold-drawability and crystallinity.

3. Crystalline Properties

The freshly precipitated polymer was found by x-ray diffraction methods to be approximately 45% crystalline, with the principal peaks occurring at 3.65 and 4.43 Å. (Fig. 5). A sample of the polymer which had been fused and allowed to crystallize at room temperature produced a similar diagram but with less broadening at the peaks. The difference in peak width is attributed to different crystallite size; the crystallites of the fused specimen were estimated to be about three times larger than those of the unmelted specimen. Both these specimens exhibited only slight crystallite orientations.

An idea of the rate of development of crystallinity in an amorphous specimen was obtained by periodically taking x-ray diagrams of the specimen as it aged at room temperature. After a freshly fused sample had cooled to room temperature, it was examined and found to be completely amorphous. No pattern emerged within the first hour but after 16 hr. the specimen was about 40% crystalline. Patterns obtained after 24 and 48 hr. indicated slight increases in crystallinity, which brought the final value to about 45%. Although the initial increase in order was due to increasing values for the maxima at both 3.65 and 4.43 Å., after 16 hr. only the latter peak contributed significantly to the increase in crystallinity.

X-ray examination of a portion of the polymer which had been fused, allowed to crystallize, and drawn into a fiber showed it to be nearly perfectly crystalline and to have a very high degree of preferred orientation (Fig. 6).

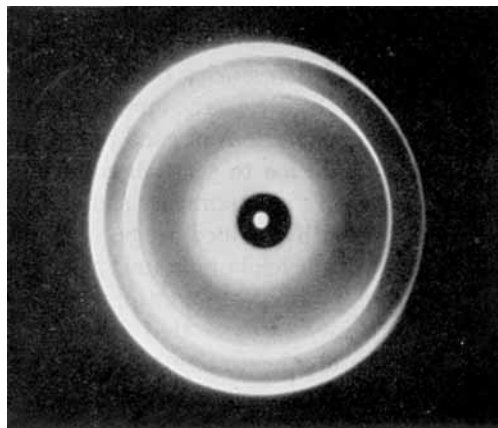


Fig. 5. X-ray diffraction pattern of unworked THF polymer.

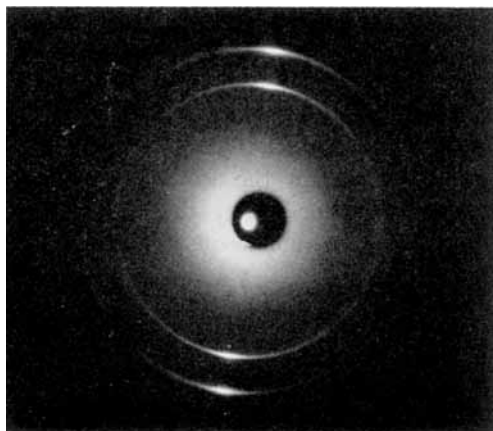


Fig. 6. X-ray diffraction pattern of fiber from THF polymer.

A particularly unusual phenomenon was observed when an amorphous sample of the polymer was quenched in liquid nitrogen. This procedure usually freezes in an amorphous structure, but when it was applied to the THF polymer the amorphous specimen crystallized at once. The x-ray pattern of the product taken immediately after quenching was practically identical with the one of a fused specimen that had crystallized slowly at room temperature. Due to this effect molded specimens could be conveniently handled at room temperature a few minutes after preparation if the mold was thoroughly cooled with Dry Ice before it was opened. Otherwise, it was necessary to allow the specimen to stand in the mold for many hours while it crystallized.

4. Mechanical Properties

Table III summarizes some of the mechanical properties of a crystalline THF polymer with an intrinsic viscosity of 3.3, which was prepared by

TABLE III
Mechanical Properties of the THF Polymer

| Property | Value | Conditions |
|------------------------------------|--------------|--|
| Ult. tens. strength, psi | 4,200 ± 300 | Stress rate: 5 in./min.; 25°C. |
| Elong. at break, % | 820 ± 40 | Cross-sect. area: 0.004 sq. in.; 25°C. |
| Mod. of elast., psi | 14,400 ± 700 | Stress rate: 0.2 in./min.; 25°C. |
| Mod. of elast. at 100% elong., psi | 1,080 ± 30 | 25°C. |
| Torsion mod., psi | 12,500 | 23°C. |
| | 10,000 | 30°C. |
| Hardness | 79 ± 3 | Shore Durometer; 25°C. |

reacting THF with 10% BF_3 at -5°C . for nine days. The relatively low tensile strength and high elongation seem to be typical of a polymer in the rubbery state although the hardness is somewhat high. These properties reflect the relatively weak interactions between adjacent chains that are expected from a polyether of the proposed structure. The readiness with which the polymer crystallizes in spite of these weak intermolecular forces lends further evidence for chain linearity.

5. Solubility

The solubility of the THF polymer in a number of common solvents is presented in Table IV.

TABLE IV
Solubility of THF Polymer

| Solvent | Soly. parameter | Hydrogen bonding capac. | Soly. ^a |
|-------------------------|-----------------|-------------------------|--------------------|
| Pentane | 7.0 | Low | — |
| Heptane | 7.4 | Low | — |
| Diethyl ether | 7.4 | Med. | + |
| Methyl isobutyl ketone | 8.4 | Med. | + |
| Carbon tetrachloride | 8.6 | Low | + |
| Acetone | 9.1 | Med. | ± |
| Benzene | 9.2 | Low | + |
| Methylene chloride | 9.7 | Low | + |
| Pyridine | 10.7 | High | + |
| <i>n</i> -Butyl alcohol | 11.4 | High | + |
| Isopropyl alcohol | 11.5 | High | — |
| Nitromethane | 12.7 | Low | — |
| Methyl alcohol | 14.5 | High | — |
| Butyrolactone | 15.5 | Med. | — |
| Water | 23.4 | High | — |

^a (+) indicates that 3 g. polymer completely dissolved in 100 ml. solvent within 24 hr. (—) indicates that 24-hr. contact with the solvent did not even cause the polymer to become tacky. (±) indicates that the polymer flowed and became slightly tacky but 3 g. did not dissolve in 100 ml. solvent in one month.

According to one theory of solubility,^{8,9} two materials will usually be miscible if they have approximately the same solubility parameter, defined as the square root of the cohesive energy density. This concept applied rather successfully to the solubility of the THF polymer despite the fact that its crystallinity is supposed to be a complicating feature. The solubility parameter of the polymer was calculated to be 8.7 from molar-attraction constants. Since the midrange of the experimental values from Table IV is 9.4, the calculated value may be somewhat low.

The only anomalous result is the one with acetone. This solvent frequently proves to be less

effective than its cohesive energy density indicates, possibly because of its exceptionally high polarity.³ Although diethyl ether and heptane have the same solubility parameter (7.4), the former is a solvent but the latter is a nonsolvent. Thus, although the dipole interactions usually show only relatively slight effects, in this case they apparently determine the solubility. At the other end of the solubility range, *n*-butyl alcohol and the polymer were compatible despite the large difference of 2.7 units between their parameters. This effect may be ascribed to the high hydrogen-bonding ability of the alcohol. When the difference between the parameters of the polymer and solvent was increased by only 0.1 unit with isopropanol, the polymer was insoluble.

Only water was found to precipitate the polymer from solution in a convenient form. The other nonsolvents produced the amorphous modification which was difficult to handle until it crystallized.

6. Thermal Properties

The crystalline melting points of all the products studied during this investigation were $41 \pm 2^\circ\text{C}$. For a given sample this transition could easily be determined as the temperature at which the compressed sample did not immediately recover when the stress was released. At this temperature there was also a well-defined visual change from an opaque, horny or leathery material to a transparent plastic mass. The polymer did not become fluid until it appeared to decompose at about 230°C .

A rather unusual criterion which was applied to the THF polymer obtained by the use of PF_5 ⁴ is the temperature at which the sample sticks to a heated metal plate. A specimen of the BF_3 -produced polymer stuck to the plate so that cohesive rupture occurred at about 220°C . This is a highly subjective test and depends to a large extent on the time of contact of the sample with the plate.

The second order transition temperature could not be determined because the polymer crystallizes so readily at low temperatures that an amorphous specimen cannot be maintained. The graph of torsion modulus versus temperature for the crystalline product fell off gradually from -80 to 35°C . without exhibiting a rapid change of slope. The polymer was pliable, although stiff, at -80 but quite brittle at -170°C .

The intrinsic viscosity and slope constant of two products were not affected by heating in air for three hours at 100°C . The constancy of these values indicates that no appreciable change occurred in

the molecular structure of the polymers as a result of the exposure.

Once ignited, the polymer burned without further heating with a nonsmoky blue and yellow flame that gave off no appreciable odor. The drippings which resulted from the combustion did not solidify on cooling or aging; they also burned to leave only a slight carbonaceous residue.

7. Effect of Irradiation

Four polymer samples were treated with cobalt 60 radiation at different dosages, two in air and two in vacuum. There was no apparent difference due to dosages in the range of 25–50 Mrep. Although air irradiation caused extensive degradation as well as crosslinking, under vacuum irradiation the polymer apparently retained most of the desirable room-temperature properties while also being crosslinked. The former product completely disintegrated into a colorless fluid on being heated to 42°C ., but at the same temperature the latter merely changed from a leathery state to a rubbery state. The rubbery form did not change up to about 170°C ., at which temperature extensive decomposition occurred. The vacuum-irradiated specimens, after aging several months in air, however, behaved just as the polymers that were irradiated in the presence of air did originally.

A sample of the THF polymer was completely degraded by exposure to ultraviolet radiation for seventy hours. The product of this reaction was a colorless fluid which did not solidify on cooling or aging. It seemed to be essentially the same material that was produced when the polymer was decomposed by heat, by oxidation, and by air irradiation.

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Synopsis

Tetrahydrofuran has been polymerized in bulk using 5–20 wt.-% BF_3 without the addition of cocatalysts to give a very high molecular weight, crystalline polymer which exhibits cold-drawability, toughness, and low temperature flexibility. Within the ranges studied a maximum conversion of 74% was reached at 10% BF_3 and 10°C. and a maximum intrinsic viscosity of 3.3 at 10% BF_3 and -5°C. Equilibrium molecular weights were obtained in about two days but the highest conversions required about an eleven day polymerization period. Structure, crystallinity, mechanical properties, solubility, thermal properties, and effect of irradiation are among the aspects of the polymer discussed.

Résumé

On a polymérisé du tétrahydrofurane en bloc en utilisant 5 à 20% de BF_3 en absence de cocatalyseurs. On obtient

un polymère cristallin de poids moléculaire élevé, qui peut être étiré à froid, résistant à la rupture et flexible à basse température. Dans le domaine étudié on a obtenu un maximum de conversion de 74% avec 10% de BF_3 à 10°C., un maximum de viscosité intrinsèque de 3.3 pour 10% BF_3 à -5°C. On a obtenu des poids moléculaires à l'équilibre en deux jours, mais les hauts degrés de conversion nécessitent une durée de polymérisation d'environ onze jours. On a étudié entr'autres la structure, la cristallinité, les propriétés mécaniques, la solubilité, les propriétés thermiques et les effets d'irradiation sur le polymère.

Zusammenfassung

Tetrahydrofuran wurde in Substanz mit 5–20% BF_3 ohne Kokatalysatorzusatz polymerisiert, um sehr hochmolekulare kristalline Polymere zu erhalten, die kalt verformbar, zäh und bei tiefen Temperaturen flexibel sind. Innerhalb des untersuchten Bereichs wurde ein maximaler Umsatz von 74% bei 10% BF_3 und 10° und eine maximale Viskositätszahl von 3,3 bei 10% BF_3 und -5° erreicht. Gleichgewichtsmolekulargewichte wurden in ungefähr zwei Tagen erhalten, für die höchsten Umsätze benötigte man jedoch eine ungefähr elftägige Polymerisationsdauer. Struktur, Kristallinität, mechanische Eigenschaften, Löslichkeit, thermische Eigenschaften und Bestrahlungseinfluss auf das Polymere werden diskutiert.

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