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# Cationic copolymerization of styrene and beta-pinene: the effect of solvent on monomer reactivity ratios

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CATIONIC COPOLYMERIZATION OF  
STYRENE AND BETA- PINENE: THE EFFECT  
OF SOLVENT ON MONOMER REACTIVITY RATIOS

by

George Yusun Paik  
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Submitted in partial fulfillment  
of the requirements for  
Honors in the Department of Chemistry

UNION COLLEGE

March, 1983

This Thesis

Submitted by

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to the

Department of Chemistry of Union College

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is approved by

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# ABSTRACT

PAIK, GEORGE YUSUN Cationic Copolymerization of Styrene and Beta- Pinene: The Effect of Solvent on Monomer Reactivity Ratios

Copolymers of styrene and B- pinene were synthesized at 30 degrees Celsius in methylene dichloride, carbon tetrachloride, and nitrobenzene. NMR analysis was used to determine the mole percent of styrene and B- pinene in the copolymer. These data were used to calculate monomer reactivity ratios in the three different solvents.

It was found that the styrene reactivity ratio increased when solvents with low dielectric constants were used. The B- pinene reactivity ratio increased as the dielectric constant of the solvent increased.

Pyrolysis and gas chromatography indicated that copolymerization may not have occurred in nitrobenzene and carbon tetrachloride if the mole percent styrene in the feed was 50% or less. However, solvent extraction with acetone on the 1:1 molar feed polymer synthesized in nitrobenzene indicated that copolymerization did occur.

## ACKNOWLEDGMENTS

During my junior year, when I was searching for a senior research topic, all the chemistry professors courteously and carefully explained to me what their research interests were. However, a certain professor spent well over an hour showing me what he had done over the past twelve years, what his equipment looked like and how it worked, and also explained the theoretical basis behind his research. I decided if a professor could spend so much time explaining his project to a prospective senior research student, imagine the amount of time he would give his actual student. Thus, for all the instruction, inspiration, guidance and patience that Dr. Howard E. Sheffer has given me, and for all the recommendations to medical schools that he wrote for me, I am extremely grateful.

I would also like to thank Susan Goldie for proofreading this thesis and for making me coffee while I was writing it.

QUOTATIONS

"Raffiniert ist der Herrgott, aber boshaft ist Er nicht"

-- Albert Einstein

"Genius is one percent inspiration and ninety- nine percent perspiration"

-- Thomas Edison

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## INTRODUCTION

Cationic polymerization is an important method of synthesizing polymers, for there are many cheap monomers that can be polymerized cationically and also a large number of Friedel-Crafts metal halides that can initiate cationic polymerization. In industry, the amount of polymers produced through cationic polymerization is second only to that of free radical-initiated polymers (1).

Two important monomers that are polymerized cationically are styrene and B-pinene. Styrene is an extremely versatile monomer, for it can be polymerized free radically and anionically as well as cationically. High molecular weight polymers of styrene, polystyrene, are widely used in the form of ice chests and other insulating devices. Low molecular weight polymers of styrene, which are produced by cationic polymerization at room temperature, are used as lacquers and resins. Styrene has been copolymerized with butadiene to make a rubber called Buna-S (2).

B-pinene is another versatile monomer. Unlike styrene, it can only be polymerized cationically. Poly-B-pinene is a low molecular weight polymer that is used primarily as the tackifier in pressure sensitive adhesives (3). B-pinene has also been cationically copolymerized with isobutylene to give a rubber which is ozone resistant and sulfur vulcanizable (4).

Recent work by Howard Sheffer and Gary Greco have shown that styrene and B-pinene definitely copolymerize in methylene dichloride at 30 degrees Celsius. The object of this author's

research was to determine the monomer reactivity ratios of styrene and B- pinene in the solvents methylene dichloride, nitrobenzene, and carbon tetrachloride. These solvents were chosen because of their different dielectric constants.

## BACKGROUND

In 1970, two papers by A. Sivola and others about the cationic polymerization of styrene and B- pinene were published. One stated that styrene and B- pinene copolymerize in m- xylene at 30 degrees Celsius (5). The other stated that when methylene dichloride was the solvent, B- pinene did not copolymerize with either styrene or isobutylene (6). Sivola's reasoning was based on evidence from Gel Permeation Chromatography and solvent fractionation of high conversion polymers. Specifically, Sivola observed a bimodal peak in the GPC chromatogram of the polymer sample that was synthesized in methylene dichloride. He used this, along with infra- red analysis, as evidence that copolymerization had not occurred. However, in 1977 Snyder, McIver and Sheffer claimed that copolymerization did occur in methylene dichloride (7). Their solvent fractionation studies strongly suggested that copolymerization had occurred. GPC evidence was inconclusive because bimodal peaks were observed even when homopolymers were studied. However, both monomers were observed in expected mole ratios when NMR was run on samples taken from the peaks.

In 1978 Sheffer, Sivola and Savalainen described the use of Curie Point pyrolysis in order to characterize the Styrene-B- pinene polymers as being copolymers (8). When the products of pyrolysis were analyzed using gas chromatography, it was discovered that the amounts of various pyrolysis products for the proposed copolymer differed from that of a mixture of homopolymers. Furthermore, solvent extraction was done on the proposed copolymers to remove any pure styrene homopolymer, and the styrene content after extraction remained essentially

the same as the polymer before extraction. These observations were strong evidence for copolymerization.

J. Kennedy and T. Chou reviewed Sivola's claim that copolymerization did not occur between B- pinene and isobutylene (4). They found that Sivola had committed an experimental error in that he had carried his polymerizations to high conversions. Kennedy and Chou stated that "the formation of heterogeneous mixtures including homopolymers and a variety of copolymers are expected to occur at medium to high conversions." This heterogeneous mixture probably accounted for the bimodal peak in Sivola's GPC. At low conversions, Kennedy and Chou observed only one peak. Thus, Sivola's use of GPC evidence was faulty, and it is clear from Kennedy's NMR evidence that in methylene dichloride and at 30 degrees Celsius, isobutylene and B- pinene copolymerize.

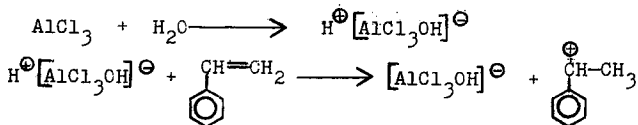
Monomer reactivity ratios were calculated by Sheffer, Sivola and Savelainen for Styrene- B- pinene copolymers made in methylene dichloride; however, their polymer yields were all greater than 10%. For accurate reactivity ratio determinations, the yields should be less than 10% (8,9). Thus, in the following set of experiments, this author's goal was to synthesize polystyrene- B- pinene copolymers, with low yields, in solvents of widely differing dielectric constants

## THEORY

Initiation of Cationic Polymerization: All polymerizations require an initiator. For cationic polymerization, the initiator must obviously cause the formation of a carbocation. The most easily visualized initiator is a strong protic acid; the carbocation is formed by the addition of the proton across the double bond of the monomer. It turns out, however, that in organic solvents, hardly any protic acids are strong enough to initiate cationic polymerization, or the gegenion is too good a nucleophile, and all that occurs is the addition of HX to the monomer.

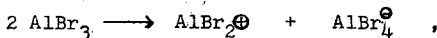
Lewis acids, which are better known as Friedels-Craft catalysts, are the most widely used initiators. Examples of these are  $\text{AlCl}_3$ ,  $\text{SnCl}_4$ , and  $\text{BF}_3$ .

In addition to the cationic initiator, many investigators of cationic polymerization believe that a coinitiator is required to start polymerization (1,2,10,11,12). The coinitiator is usually a protic substance, such as water. An example of initiation is the following:



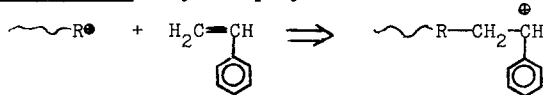
The concentration of coinitiator required is very minute; it is on the order of  $10^{-5}$  M. Addition of too much coinitiator lowers the yield of polymer, for large amounts of coinitiator will hydrolyze the Friedels-Craft initiator. Excessive concentrations of coinitiator also reduces the molecular weight of the polymer (13).

There is considerable skepticism on whether a coinitiator is indeed necessary for cationic polymerization. Aluminum bromide functions as its own coinitiator:

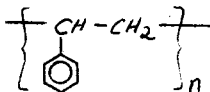


and the cation,  $\text{AlBr}_2^{\oplus}$ , initiates polymerization (12). However, in order to disprove the need for a coinitiator, all reagents must be thoroughly dried, all impurities must be removed, and the polymerization must be run in a dry box. Most experiments that have "proved" that no coinitiator is required have been shown to be in error (12). In any event, in the copolymerizations conducted by this author, sufficient traces of water were present which could have functioned as a coinitiator.

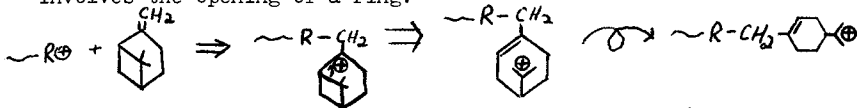
Propagation: Styrene polymerizes in the following way:



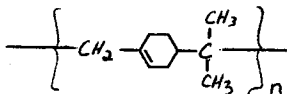
The benzylic secondary carbocation is very stable. The following is the repeat unit of polystyrene:



The polymerization of B-pinene is more complex, for it involves the opening of a ring:

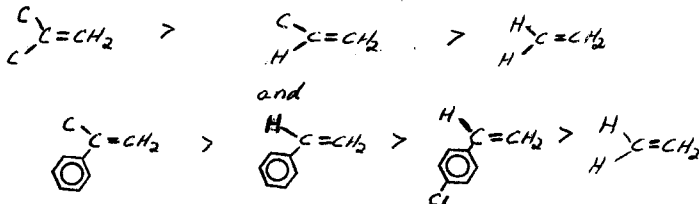


The repeat unit of poly-B-pinene is at least 50% of the following:

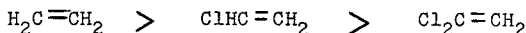


Successful propagation of B-pinene is due to three factors. One is the formation of a tertiary cation; the second is the fact that the double bond of B-pinene is a very reactive exomethylene double bond; and the third is that the opening of the cyclobutane ring relieves strain (1,3).

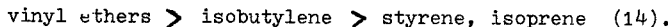
In general, reactivity of double bonds in cationic polymerization depends on the electron donating characteristics of the double bond. The more electron donating, the higher the reactivity. The following ranks reactivities:



Electronegative substituents decrease the electron density of the double bond, thus decreasing the cationic reactivity (12).



Based on sparse quantitative data, the following reactivity order has been observed:



Steric factors often affect reactivities of cationic polymerization. Consider the following two double bonds:



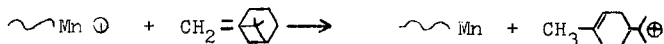
Due to the extra carbon, "Y" has the greater electron density and should be more reactive. However, "X" polymerizes much faster. This can only be rationalized by steric factors. For this reason, B-pinene which has two hydrogens on its terminal alkene carbon, is more reactive than alpha-pinene (3).

Termination: The addition of large quantities of a protic solvent to any cationic polymerization will quench, or permanently terminate the reaction. Methanol is commonly used for quenching, for it is miscible with most organic solvents. The process of quenching is described below:



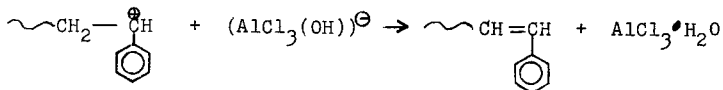
Methanol will also hydrolyze any remaining cationic initiator.

There are other reactions present during propagation that will terminate the growth of a polymer chain. One is proton transfer to a monomer:



Cationic polymerizations done at room temperature yield low molecular weight polymers primarily because of proton transfer to the monomer. Proton transfer becomes less significant with lower temperatures; thus, high molecular weight polymers are obtained at temperatures of  $-100^{\circ}\text{C}$  or less (13).

A second termination reaction is the proton transfer to the gegenion formed in the initiation step:

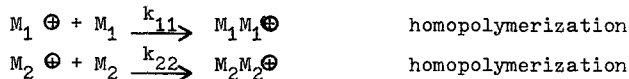


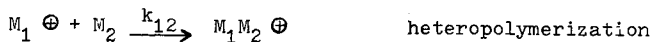
Although it is well- established that the yield of polymer increases with initiator concentration, it is desirable to add the initiator in small portions. Among other factors, this minimizes proton transfer to the negative ion of the initiator, and keeps the molecular weight of the polymer from being lowered.

Another termination reaction is the reaction of the polymer chain with coinitiator. If the coinitiator concentration is present in concentrations greater than trace amounts, the carbocation of the polymer chain will react with the coinitiator, terminating chain growth and lowering molecular weight. It has been shown that addition of 0.1 M HCl to a cationic polymerization system causes a tenfold reduction in the molecular weight (13).

Finally, impurities may also terminate cationic polymerization. For example, B- pinene must be carefully purified to remove alpha- pinene, for alpha- pinene may function as a poison and halt growth of the chain (3).

Monomer Reactivity Ratios of Copolymers: The general copolymer equation was developed by Alfrey, Dostal, Ham, Mayo, Simha and Wall (9). This equation is valid for all types of copolymerizations. Two assumptions are made about the reactivities of carbocations. One is that the reactivity of the cationic end of the polymer is independent of chain length. The second is that reactivity is solely determined by the terminal unit. There are four propagating reactions which determine rates:





The mole fractions of  $M_1$  and  $M_2$  that are incorporated into the copolymer chain are designated by  $F_1$  and  $F_2$ . They are related to the rate of disappearance of  $M_1$  and  $M_2$  in the feed:

$$F_1 = \frac{-[M_1]}{dt} = k_{11} [M_1 \oplus] [M_1] + k_{21} [M_2 \oplus] [M_1]$$

$$F_2 = \frac{-d[M_2]}{dt} = k_{22} [M_2 \oplus] [M_2] + k_{12} [M_1 \oplus] [M_2]$$

During the early stages of the reaction, one can assume that the rate of conversion of  $M_1 \oplus$  to  $M_1 M_2 \oplus$  is equal to the rate of conversion of  $M_2 \oplus$  to  $M_2 M_1 \oplus$ . This is a steady-state assumption. Without this assumption, i.e., if the conversion of  $M_2 \oplus$  to  $M_2 M_1 \oplus$  was greater, there would be a buildup of  $M_1 \oplus$ . With the steady-state assumption,

$$k_{21} [M_2 \oplus] [M_1] = k_{12} [M_1 \oplus] [M_2]$$

We now define the monomer reactivity ratios:

$$r_1 = \frac{k_{11}}{k_{12}} \quad \text{and} \quad r_2 = \frac{k_{22}}{k_{21}}$$

or in general,  $r = \frac{\text{rate of homopolymerization}}{\text{rate of heteropolymerization}}$

$$\text{Now, } \frac{F_1}{F_2} = \frac{k_{11} [M_1 \oplus] [M_1] + k_{21} [M_2 \oplus] [M_1]}{k_{22} [M_2 \oplus] [M_2] + k_{12} [M_1 \oplus] [M_2]}$$

Combining the steady-state assumption and the monomer reactivity ratio with the last equation, one obtains the following:

$$\frac{F_1}{F_2} = \frac{r_1 \left\{ \frac{[M_1]}{[M_2]} \right\} + 1}{r_2 \left\{ \frac{[M_2]}{[M_1]} \right\} + 1} \quad \text{The General Copolymer Equation}$$

Let  $x = M_1/M_2$ , the composition of the feed, and  $n = F_1/F_2$ , the composition of the copolymer. Then

$$n = \frac{r_1 x + 1}{r_2/x + 1}$$

If one knows the monomer reactivity ratio, one can control the composition of the copolymer by manipulating the value of  $x$ .

In order to find  $r_1$  and  $r_2$ , conversions should be ten per cent or less.

The monomer reactivity ratios can be used to characterize the type of copolymer formed. If  $r_1 r_2 = 1$ , there is perfect randomness. This is known as ideal copolymerization. If  $r_1 r_2 = 0$ , the polymer exhibits perfect alternation. The polymer would then have the following structure:



The product of  $r_1$  and  $r_2$  is used to estimate the extent of randomness.

If  $r_1 r_2 > 1$ , there is a tendency towards block or homopolymerization. If both  $r_1$  and  $r_2$  are greater than 1, there is a tendency for block polymerization (long sequences of each monomer in the chain). The copolymer equation is not valid for steric or polar restrictions (9).

In order to determine monomer reactivity ratios, polymers with different feed ratios must be synthesized. Monomer content is then determined, and a graphical method developed by T. Kelen and F. Tudos is used to determine the monomer reactivity ratios. The Kelen- Tudos method is described in the Appendices (15,16,17).

Solvent Effects: In contrast to free- radical copolymerization, solvent plays a major role in determining monomer reactivity ratios in cationic copolymerization. Data from the literature show that the rate of polymerization increases as the dielectric constant of the solvent increases (9). The amount of increases of course depends on the monomer and the initiator. The rate of polymerization depends on the concentration of free cation in solution; thus, if the solvent has good solvating power, the cation will be more stabilized, the concentration of the cation will increase, and the rate of polymerization will also increase. The dielectric constant of the solvent is a useful, but incomplete method of characterizing solvating power. Size, shape and polarizability of the solvent molecule are also important considerations. An interesting phenomena occurs when solvents of low **solvating** power, like carbon tetrachloride, are used. If the monomer is polarizable, the monomer will take part in the solvating of the cation. Thus, the rate order of styrene is two when cationically polymerized in benzene, but is three in carbon tetrachloride (14).

It was previously mentioned that since solvating power of the solvent greatly affects the rate of polymerization, the choice of solvent should also affect the monomer reactivity ratios in cationic copolymerization. This is clearly indicated in the cationic copolymerization of isobutylene and *p*- chlorostyrene with  $\text{AlBr}_3$ . In hexane, a solvent with a low dielectric constant, the ratios were approximately one. However, in nitrobenzene, the reactivity ratio for isobutylene is 14.7, for *p*- chloro-

styrene, 0.15 (18). Similiar results can be expected with styrene and B- pinene.

Pyrolysis: Cationically polymerized polystyrene made in methylene dichloride possesses good thermal stability compared to poly-B- pinene. Thus, pyrolysis of polymers seems to be a good method of determining whether a sample is a true copolymer or a mixture of homopolymers. Poly- B- pinene thermally decomposes via "cracking"- heating will cause the weaker bonds to break, giving terpenes as the pyrolysis product (19). Polystyrene, on the other hand, thermally decomposes by "unzipping"- once a carbon- carbon single bond is broken, the resulting radical will "unzip" the styrene units off, giving mostly styrene as the pyrolysis product (19). If a 1:1 molar mixture of homopolymers is pyrolyzed at 500°C and if the pyrolysis products are sent into a gas chromatograph, more poly- B- pinene will decompose than polystyrene, and one obtains a low styrene- to- terpene ratio. If a copolymer is pyrolyzed at 500°C, radicals are formed by the cracking of the B- pinene portion, and these radicals proceed to unzip the styrene portion. The result is a much higher styrene- to- terpene ratio for the copolymer than for a mixture of homopolymers.

## EXPERIMENTAL

Materials:

	molec. wt.(g)	M.P.(°C)	B.P.(°C)	Density (g/ml)	Dielectric Constant, 25°C
CH <sub>2</sub> Cl <sub>2</sub>	84.93	-95.1	40	1.3266	9.08
CCl <sub>4</sub>	153.82	-23.0	76.5	1.5940	2.23
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	123.11	+5.7	210.8	1.2037	34.82
Styrene	104.16	-30.6	145.2	0.9060	2.43
B- pinene	136.24	....	164	0.8694	2.64
AlCl <sub>3</sub>	133.34	+190	....	2.44	7.0

B- pinene was purified in Finland by vacuum distillation. Purity was over 99%. This purity was recently rechecked with GC. Nitrobenzene was purified by distillation and dried over molecular sieves. Carbon tetrachloride, methylene dichloride and styrene were used as received.

In order to determine monomer reactivity ratios in polymers, copolymers with different molar feed ratios were synthesized. Conversions of less than 10% were desired. Total monomer concentration was 25% molar. The amount of AlCl<sub>3</sub> used was adjusted to give 10% yields or less.

## Copolymers Synthesized in Methylene Dichloride

Sample #	601, 1601	602, 1602	603, 1603	604, 1604	605, 1605
Styrene: B- pinene	50:50	20:80	35:65	65:35	80:20
Styrene (g)	6.2	2.5	4.4	8.1	10.0
B- pinene (g)	8.2	13.0	10.6	5.7	3.25
CH <sub>2</sub> Cl <sub>2</sub> (g)	30.6	30.6	30.6	30.6	30.6
AlCl <sub>3</sub> (g)	0.04	0.04	0.04	0.04	0.04

## Copolymers Synthesized in Nitrobenzene

Sample #	701	702	703	704	705
Styrene: B- pinene	50:50	20:80	35:65	65:35	80:20
Styrene (g)	3.1	1.25	2.2	4.05	5.0
B- pinene (g)	4.1	6.5	5.3	2.85	1.625
$C_6H_5NO_2$ (g)	22.2	22.2	22.2	22.2	22.2
$AlCl_3$ (g)	0.04	0.04	0.04	0.04	0.04

## Copolymers Synthesized in Carbon Tetrachloride

Sample #	801	802	803	804	805
Styrene: B- pinene	50:50	20:80	35:65	65:35	80:20
Styrene (g)	3.1	1.25	2.2	4.05	5.0
B- pinene (g)	4.1	6.5	5.3	2.85	1.625
$\text{CCl}_4$ (g)	27.7	27.7	27.7	27.7	27.7
$\text{AlCl}_3$ (g)	0.05	0.05	0.05	0.05	0.05

### Synthesis of Copolymer

The proper masses of monomers and solvent were placed in either a 250 ml or 500 ml three-neck, round bottom flask. The flask and its contents were placed in a 30°C constant temperature bath. Nitrogen was bubbled through pure solvent and introduced into the flask, providing an inert atmosphere. A glass stirrer with a teflon blade was inserted in the middle neck. A condenser was attached to the third neck. After allowing the contents of the flask to come to 30°C, the  $\text{AlCl}_3$  was added all at once. A slight color change was observed. The polymerization was run from 30 to 60 minutes. At this point, three different techniques were used to isolate the copolymer. In each technique, the polymer was precipitated twice.

Procedure 1: The reaction mixture was poured into a beaker containing about 250 ml of methanol. This quenched the polymerization and also precipitated the polymer. The solution was then suction filtered. The filtrate was redissolved in either 10 ml of hot benzene or toluene. This solution was added dropwise to about 200 ml of methanol that was being magnetically stirred. The methanol was suction filtered, and the polymer was isolated as a fine white powder. The problem with this procedure was that when the polymer was initially suction filtered, the filter paper very quickly became gummed and clogged, preventing any more polymer from being filtered. It is conceivable that much polymer was lost via this technique.

Procedure 2: An additional step was inserted into Procedure 1. After the polymer was initially precipitated, the methanol-polymer mixture was heated to boiling for several minutes.

Polymer was observed to collect on the walls of the beaker; the polymer was found to be very stringy and sticky in this condition. When no more polymer was observed to collect on the wall of the beaker, the contents of the beaker were cooled, and the liquid portion was carefully decanted. The remaining polymer, which was still stuck to the wall, was dissolved in hot benzene or toluene and reprecipitated. It is the belief of this author that little polymer was lost in this procedure.

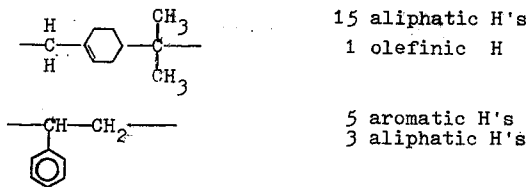
Procedure 3: No more than 5 ml of methanol was poured into the three-neck flask. This amount of methanol is sufficient to quench the reaction, but will not precipitate any polymer. The reaction mixture was then added dropwise to about 250 ml of methanol. The methanol was again magnetically stirred. The polymer precipitated in the form of a fine white powder. The polymer was suction filtered, allowed to dry, redissolved in 10 ml of hot benzene or toluene, and reprecipitated in methanol. This procedure proved to be superior to the first two, for during suction filtration, the filter paper never clogged. This procedure also proved to be faster, and it is the belief of the author that the least amount of polymer was lost using this procedure.

It is the author's opinion that none of these procedures affected the monomer content of the copolymer.

After the second precipitation, the copolymer was washed with methanol and dried in a vacuum oven for three to four hours to remove any remaining benzene or toluene.

Determination of Copolymer Content

NMR was used to determine molar percent of styrene and B-pinene in the copolymer. The NMR used was the Hitachi Perkin-Elmer High Resolution NMR Spectrometer R-24 A. Due to the broad NMR peaks of the polymer, a considerable amount of sample was required in the sample tube. In all cases, TMS was the reference,  $\text{CCl}_4$  was the solvent, and the sweep time was 300 seconds. The following repeat units are found in poly (styrene-B-pinene) polymer:



Let  $s$  = mole percent of styrene in the copolymer.

Let  $p$  = mole percent of B-pinene in the copolymer.

$5s \sim$  area of aromatic peak

$3s + 15p \sim$  area of aliphatic peak

-thus-

$$\frac{5s}{3s + 15p} = \frac{\text{area of aromatic peak}}{\text{area of aliphatic peak}} = \frac{\text{Ar}}{\text{Al}}$$

since  $s+p=100$ ,  $p=100-s$  and

$$\frac{5s}{3s + 15(100 - p)} = \frac{\text{Ar}}{\text{Al}}$$

solving for  $s$ ,

$$\text{mole percent styrene} = \frac{1500 \text{ Ar}}{5\text{Al} + 12\text{Ar}}$$

Sample	% yield	mole % styrene, feed	Ar	Al	Amplitude		mole % styrene, polymer
					Spectrum	Integral	
601	3.4	50	9.8	58	9	5	36.1
602	2.2	20	3	60.5	7	4	13.3
603	4.7	35	9.9	59.6	9	4	35.6
604	20.1	65	21	52	9	5	61.5
605	12.6	80	37.4	53	9	5	82.6
1601	8.4	50	10.5	53	10	6	40.3
1602	7.7	20	5	74.5	7	4	17.3
1603	5.0	35	6.9	67.5	9	5	24.6
1604	13.2	65	31.5	76.0	9	5	62.3
1605	11.6	80	41.5	57	9	6	79.5
701	4.6	50	9	66.5	11	8	30.6
702	4.6	20	2.5	73.5	9	6	9.4
703	3.7	35	10.5	77	14	8	30.8
704	7.5	65	23.5	73	13	7	54.5
705	9.7	80	40	68	14	8	73.2
801	3.6	50	22	65	12	7	56.0
802	2.5	20	7	70	10	6	24.2
803	2.7	35	11	59	13	7	38.6
804	7.1	65	30	49.5	9	6	74.1
805	8.2	80	38	37	9	6	88.9
Finland							
J3	19	50					42
J1	20	20					17
J2	13	33					31
J4	19	67					62
J5	15	80					77

## Monomer Reactivity Ratios

Sample Series #	Solvent	r(styrene)	r(B-pinene)	Correlation
800	$\text{CCl}_4$	1.56	0.90	0.978
Finland	$\text{CH}_2\text{Cl}_2$	0.78	1.17	0.986
600	$\text{CH}_2\text{Cl}_2$	1.08	1.57	0.879
1600	$\text{CH}_2\text{Cl}_2$	0.92	1.31	0.967
700	$\text{C}_6\text{H}_5\text{NO}_2$	0.90	2.75	0.982

Copolymer samples were synthesized in Finland, but conversions were all greater than 10%. Thus, low conversion copolymers samples were resynthesized in methylene dichloride. However, the first set of samples (601- 605) gave poor results, as indicated by the correlation. Thus, samples were synthesized a third time and given the series number 1600. These gave much better correlation.

Solvent Extraction: Solvent extraction with acetone was performed to determine if copolymerization had occurred, or if the copolymer was in actuality a mixture of homopolymer. One hundred ml of acetone were placed in a one-neck round bottom flask. A condenser was set up for reflux. An extraction thimble ~~containing~~ polymer was lowered through the condenser and was supported with copper wire. The thimble was positioned such that the acetone that condensed in the condenser would drip into the thimble. The acetone was heated to boiling and refluxed for thirty minutes. Solvent extraction was run on sample 701, the 50:50 molar feed synthesized in nitrobenzene.

Weight of sample before extraction = 0.1408 g  
 after extraction = 0.0967 g

amount of sample extracted = 0.0441 g  
 = 31.3%

Styrene content of 701 before extraction = 30.6%  
 after extraction = 23.3%

Pyrolysis

All copolymers synthesized in nitrobenzene or carbon tetrachloride were pyrolyzed. Equimolar mixtures of homopolymers were prepared and pyrolyzed. The styrene to terpene ratios for homopolymers were calculated from the equimolar mixture.

Sample	%styrene, feed	%styrene polymer	styrene/ terpene
702	20	9.4	0.20
703	35	30.8	*0.32
701	50	30.6	0.66
704	65	54.5	*1.05
705	80	73.2	0.60
1:1 mixture			*1.04
			2.12
			*1.85
			8.7
			*2.5
			1.7
802	20	24.2	0.53
803	35	38.6	*1.73
801	50	56.0	1.6
804	65	74.1	*2.76
805	80	88.9	2.74
1:1 mixture			*4.01
			9.8
			*5.31
			41.6
			*6.37
			3.58

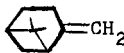
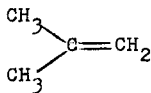
\*calculated from 1:1 mixture  
of homopolymers

## DISCUSSION

Before one calculates monomer reactivity ratios, one must indeed determine whether or not one truly has a copolymer. Two previously successful methods for determining copolymerization have been pyrolysis and solvent extraction. Both methods were used to prove that styrene and B- pinene do copolymerize in methylene dichloride. Let us examine the pyrolysis data for polymers made in nitrobenzene and carbon tetrachloride. It was previously stated that evidence for copolymerization was that pyrolysis of the copolymer yielded a higher styrene to terpene ratio than a mixture of homopolymers. Using this criterion, only samples 704, 705, 804 and 805 seem to have copolymerized. These are samples which have 65% or 80% styrene in the feed. According to pyrolysis, the samples with less than 65% styrene in the feed did not seem to copolymerize. Solvent extraction on sample 701 ( 50 mole% styrene in the feed), however, removed only a small portion of the styrene. This indicates that 701 is indeed a copolymer. The contradiction is resolved upon reexamination of the pyrolysis data. When the equimolar mixture of homopolymers was pyrolyzed, the styrene to terpene ratio was determined to be greater than one for polymers made in both nitrobenzene and in carbon tetrachloride. This indicates that polystyrene is less thermally stable than poly-B- pinene. However, it is almost universally accepted that polystyrene is a thermally stable polymer and poly-B- pinene is not. Thus, all the data from pyrolysis of the 700 and 800 series of samples are suspect and no conclusion about copolymerization can be made from the pyrolysis of these samples.

### The Effect of Solvent on Monomer Reactivity Ratios

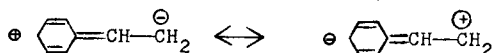
The cationic copolymerization of styrene and B- pinene were done in three different solvents. These solvents- methyl-ene dichloride, nitrobenzene, carbon tetrachloride- were select-ed for several reasons. One is because of their different di-electric constants. As organic solvents go, carbon tetrachlo-ride has one of the lowest dielectric constants, nitrobenzene has one of the highest, and methylene dichloride has an inter-mediate value. Another reason is that all three solvents are relatively inert to carbocations. Examination of the monomer reactivity ratios shows that B- pinene has highest reactivity in the solvent with the highest dielectric constant, while styrene has greatest reactivity in the solvent with the lowest dielectric constant. Earlier in this report, it was stated that isobutylene was observed to be more reactive than styrene (14). Consider the similarity between isobutylene and B- pinene:



B- pinene indeed should be more reactive than isobutylene, for accompanying the formation of the tertiary carbocation is the opening of a strained ring. B- pinene should thus be much more reactive towards cationic copolymerization than styrene. However, this is true only in nitrobenzene and methyl-ene dichlo-ride.

What must also be considered is the greater solvating power of styrene over B- pinene. Even though styrene has a

slightly lower dielectric constant than B- pinene, styrene is much more polarizable. Because of its aromatic ring, styrene has the following as two possible resonance structures:



Both structures have approximately the same stability, thus accounting for the fact that styrene has a very small permanent dipole moment (20). However, if a positive charge were brought close to styrene, one would expect to observe shifting of electron density in the pi- electron system. B- pinene, however, is a poorer solvator of cations. It is much less polarizable, and while styrene is a flat molecule, B- pinene, being a bicyclic terpene, is very bulky. We thus have a confrontation between reactivity and solvating power; the choice of solvent will determine which effect will "win out."

Carbon Tetrachloride: In  $\text{CCl}_4$ , the reactivity ratio of styrene is 1.56, and for B- pinene, 0.90. This is due to the fact that styrene competes effectively against  $\text{CCl}_4$  in solvating carbocations. Carbon tetrachloride is a large, non- polar molecule; it is not easily polarized. It thus does not solvate carbocations well. A carbocation is therefore solvated by  $\text{CCl}_4$  and styrene molecules, and because of the proximity of the styrene molecule to the cation of the growing polymer chain, a greater amount of styrene will be incorporated into the copolymer. This explains why styrene in  $\text{CCl}_4$  has a reactivity ratio greater than one.

B- pinene, however, is almost totally excluded from the

solvation cage of the carbocation. In order to react with the cation, a B- pinene molecule must displace either a  $\text{CCl}_4$  or a styrene molecule. Since B- pinene is separated from the carbocation by the solvation cage, its reactivity ratio in  $\text{CCl}_4$  is less than one.

Nitrobenzene: Nitrobenzene is polarizable because of its aromatic ring, and it has a large dipole moment due to the positive charge on the nitrogen. Because of these factors, nitrobenzene has a large dielectric constant (20). Because styrene possesses no permanent dipole moment, nitrobenzene is a much better solvator of carbocations. Thus, when styrene and B- pinene are copolymerized in nitrobenzene, the solvation cage surrounding the carbocation of the polymer consists almost entirely of nitrobenzene molecules. For either B- pinene or styrene to react with the growing polymer, they must penetrate this solvation cage. Since B- pinene is bulkier than styrene, fewer B- pinene molecules would penetrate the cage than styrene molecules. However, the dominant factor is the greater reactivity of B- pinene. For these reasons, in nitrobenzene, B- pinene has a significantly greater reactivity ratio than styrene.

Methylene Dichloride:  $\text{CH}_2\text{Cl}_2$  has a large dipole moment, but it is not very polarizable. Therefore, while  $\text{CH}_2\text{Cl}_2$  is a fairly good solvator of carbocations, it is not as good as nitrobenzene. In cationic copolymerization, the solvation cage probably consists of mostly  $\text{CH}_2\text{Cl}_2$ , but with small amounts of styrene. Thus, while the reactivity ratio of B- pinene is still greater than styrene, the difference is not as large as in  $\text{C}_6\text{H}_5\text{NO}_2$ .

## CONCLUSION

B- pinene forms a carbocation more readily than styrene. Styrene is a better solvator of carbocations than B- pinene. Because of these factors, solvent choice in the cationic copolymerization of styrene and B- pinene greatly affects monomer reactivity ratios.

Pyrolysis indicated that in nitrobenzene and in carbon tetrachloride, copolymerization may not have occurred when mole percent styrene in the feed was fifty percent or less. Solvent extraction, however, indicated that a copolymer in nitrobenzene was formed when the styrene content in the feed was fifty percent.

Pyrolysis of a one to one molar mixture of homopolymers synthesized in nitrobenzene or carbon tetrachloride gave a styrene to terpene ratio greater than one. The validity of the pyrolysis data was questioned, since this indicated that the polystyrene is thermally less stable than poly- B- pinene.

## SUGGESTIONS FOR FUTURE RESEARCH

- 1) Perform Solvent Extraction on all polymers synthesized in nitrobenzene and in carbon tetrachloride in order to determine if copolymerization did occur.
- 2) Use  $\text{SnCl}_4$  or  $\text{AlBr}_3$  as the catalyst.
- 3) Use either p- chlorostyrene or alpha- methylstyrene instead of styrene.
- 4) Investigate low temperature copolymerization ( $-100^\circ\text{C}$ ) and determine monomer reactivity ratios

## APPENDICES

I) Calculating Monomer Reactivity Ratios

Once the monomer content of the copolymers is determined, the Kelen- Tudos method is used to determine monomer reactivity ratios. The Kelen- Tudos method is a linear graphical method for determining reactivity ratios.

## Procedure:

- 1) Find the mole percent in the feed of one monomer, and find the mole percent in the polymer of the same monomer.
- 2) Let  $x = \frac{\text{feed}}{1 - \text{feed}}$  and  $y = \frac{\text{polymer}}{1 - \text{polymer}}$
- 3) Let  $F = \frac{x^2}{y}$  and  $G = \frac{x(y - 1)}{y}$
- 4) Let  $\alpha = \sqrt{F_1 + F_5}$
- 5) Let  $\eta = \frac{G}{\alpha + F}$  and  $\xi = \frac{F}{\alpha + F}$
- 6) Graph  $\eta$  versus  $\xi$
- 7) When  $\xi = 0$ ,  $\eta = -r_2/\alpha$  . When  $\xi = 1$ ,  $\eta = r_1$  .
- 8) Thus,  $r_1 = \eta_1$  and  $r_2 = -\eta_0 \cdot \alpha$

(33)

Sample	Feed	Polymer	x	y	F	G	$\bar{r}$	$\bar{z}$	$\alpha$
602	20	13.3	.25	.153	0.408	-1.384	-0.875	0.258	1.173
603	35	35.6	.538	.533	0.543	-0.471	-0.274	0.316	
601	50	36.1	1.0	.565	1.770	-0.770	-0.262	0.601	
604	65	61.5	1.857	1.597	2.159	0.694	0.208	0.648	
605	80	82.6	4.0	4.747	3.371	3.157	0.695	0.742	
1602	20	17.3	.25	.209	0.299	-0.946	-0.671	0.212	1.111
1603*	35	24.6	.538	.326	0.888	-1.112	-0.556	0.444	
1601	50	40.3	1.0	.675	1.481	-0.481	-0.186	0.571	
1604	65	62.3	1.857	1.653	2.086	0.734	0.230	0.652	
1605	80	79.5	4.0	3.878	4.126	2.969	0.567	0.788	
702	20	9.4	.25	.104	0.601	-2.154	-0.869	0.243	1.877
703*	35	30.8	.538	.445	0.650	-0.671	-0.266	0.257	
701	50	30.6	1.0	.441	2.268	-1.268	-0.306	0.547	
704	65	54.5	1.857	1.198	2.879	0.307	0.065	0.605	
705	80	73.2	4.0	2.731	5.859	2.535	0.328	0.757	
802	20	24.2	.25	.319	0.196	-0.534	-0.783	0.287	0.496 <sup>2</sup>
803	35	38.6	.538	.629	0.460	-0.317	-0.335	0.486	
801	50	56.0	1.0	1.273	0.786	0.214	0.163	0.618	
804	65	74.1	1.857	2.861	1.205	1.208	0.714	0.713	
805*	80	88.9	4.0	8.009	1.998	3.501	----	----	
Finland									
J1	20	17	.25	.205	.305	-0.970	-0.642	0.202	1.207
J2	33	31	.493	.449	.541	-0.605	-0.346	0.309	
J3	50	42	1.0	.724	1.381	-0.381	-0.147	0.534	
J4	67	62	2.03	1.632	2.525	0.786	0.211	0.677	
J5	80	77	4.0	3.348	4.779	2.805	0.469	0.798	

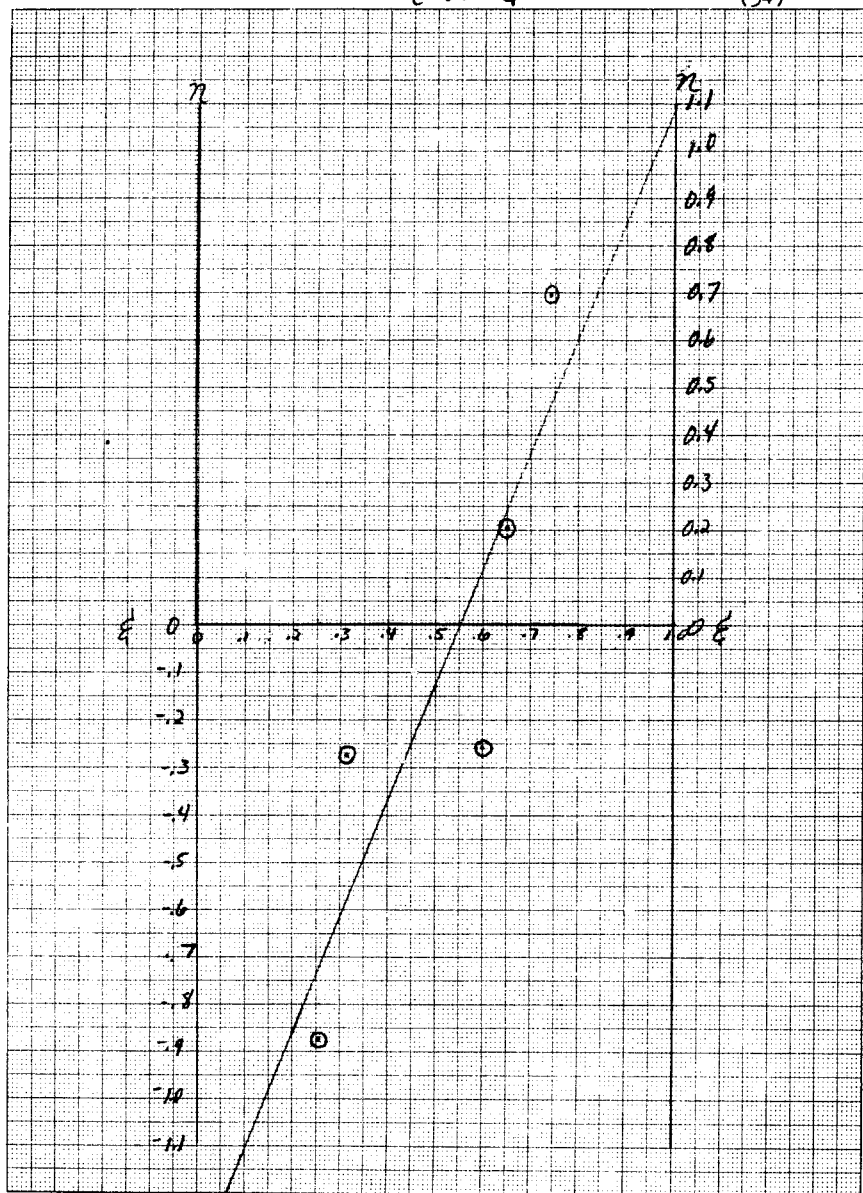
\*These data points were thrown out.

$$^2 \alpha = \sqrt{F_1 \cdot F_4}$$

600

 $\eta$  vs.  $\xi$ 

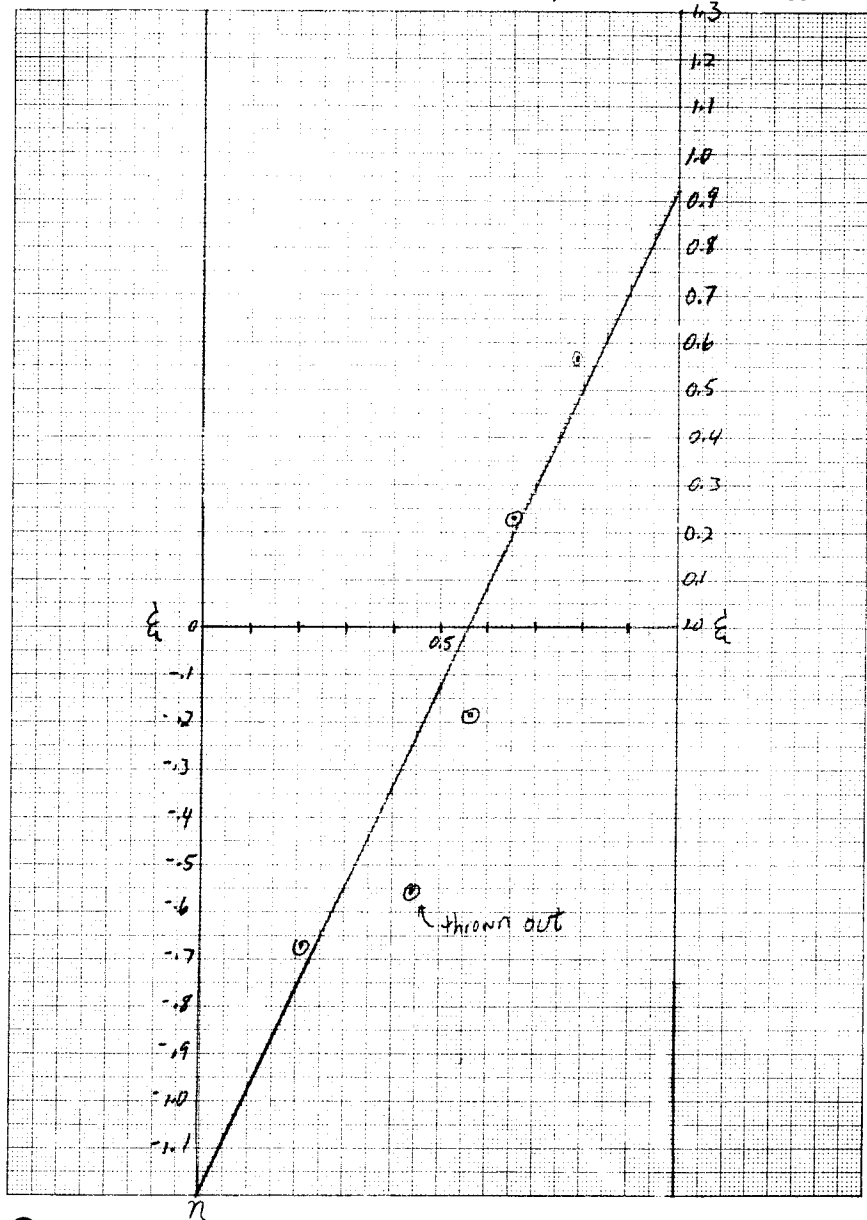
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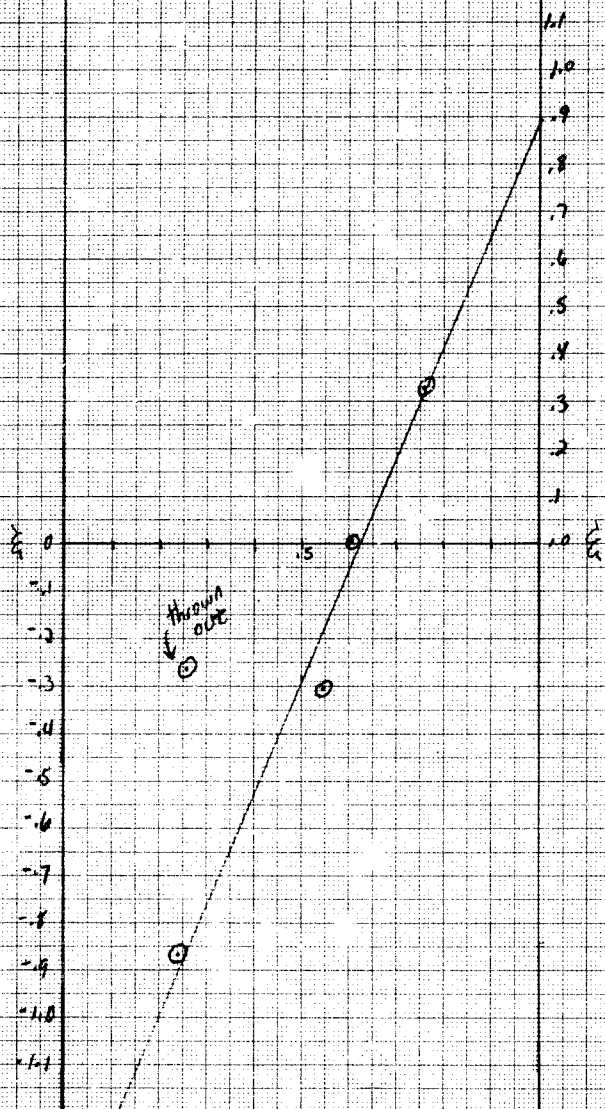


1600

 $\eta$  vs.  $\xi$  $\eta$ 

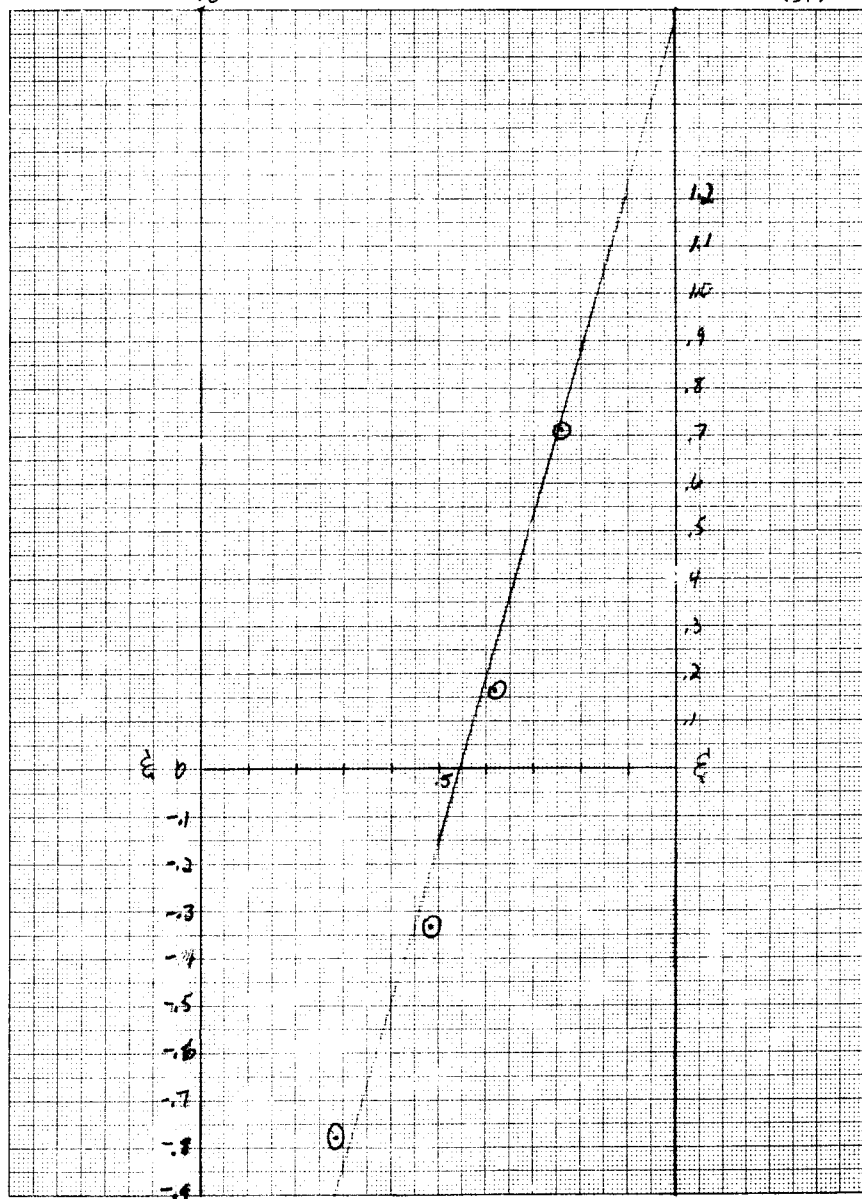
(35)



$n$ 700  $n$  vs  $E$  $n$  (36)

$n$  800  $n$  vs  $\xi$

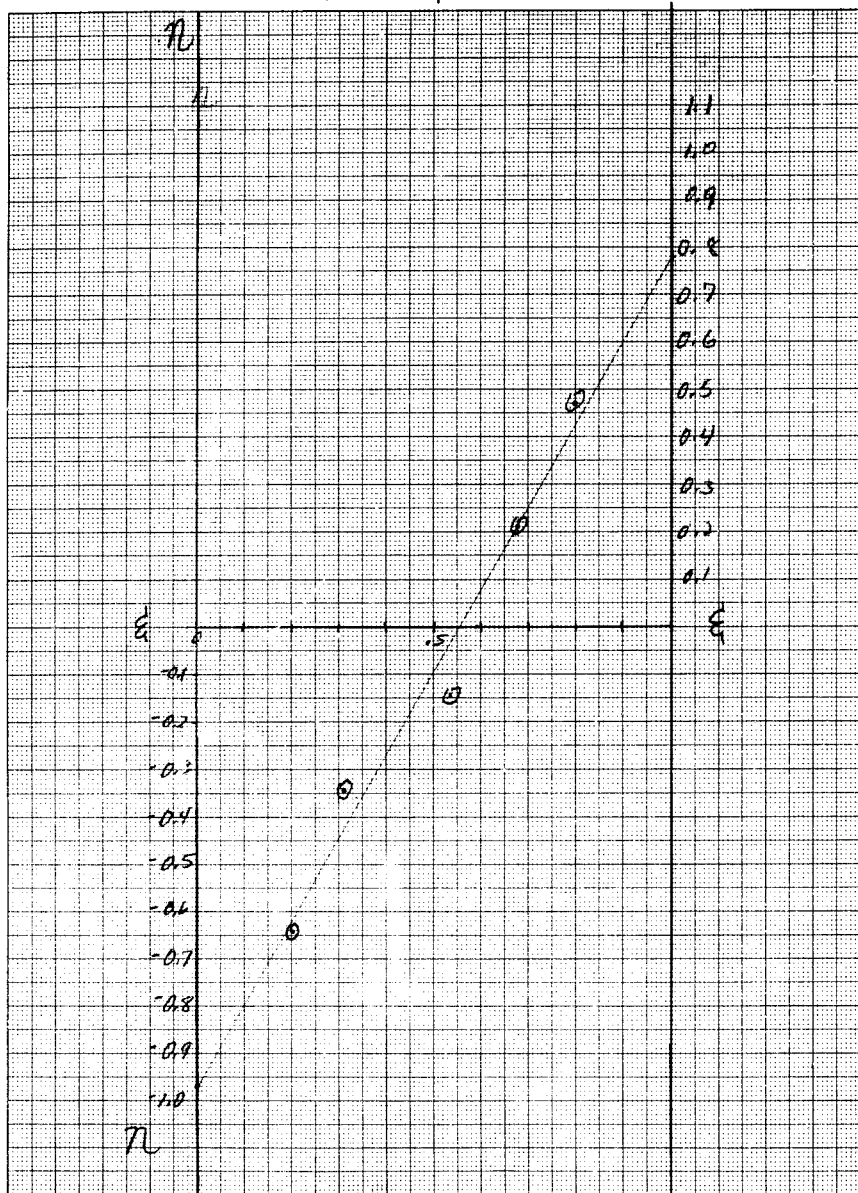
$n$  (37)



# Finland Samples

2

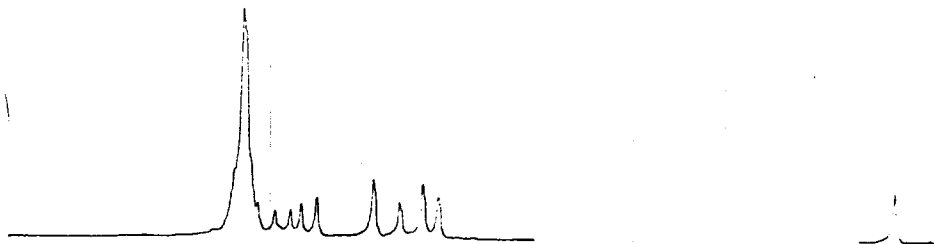
(38)



600	corr. = 0.879		
	$\xi = 0$	$\eta = -1.34$	$r_2 = 1.57$
	$\xi = 1$	$\eta = 1.08$	$r_1 = 1.08$
1600	corr. = 0.967		
	$\xi = 0$	$\eta = -1.183$	$r_2 = 1.31$
	$\xi = 1$	$= 0.919$	$r_1 = 0.92$
700	corr. = 0.982		
	$\xi = 0$	$\eta = -1.47$	$r_2 = 2.75$
	$\xi = 1$	$\eta = 0.90$	$r_1 = 0.90$
800	corr. = 0.978		
	$\xi = 0$	$\eta = -1.86$	$r_2 = 0.90$
	$\xi = 1$	$\eta = 1.56$	$r_1 = 1.56$
Finland	corr. = 0.986		
	$\xi = 0$	$\eta = -0.973$	$r_2 = 1.17$
	$\xi = 1$	$\eta = 0.777$	$r_1 = 0.78$

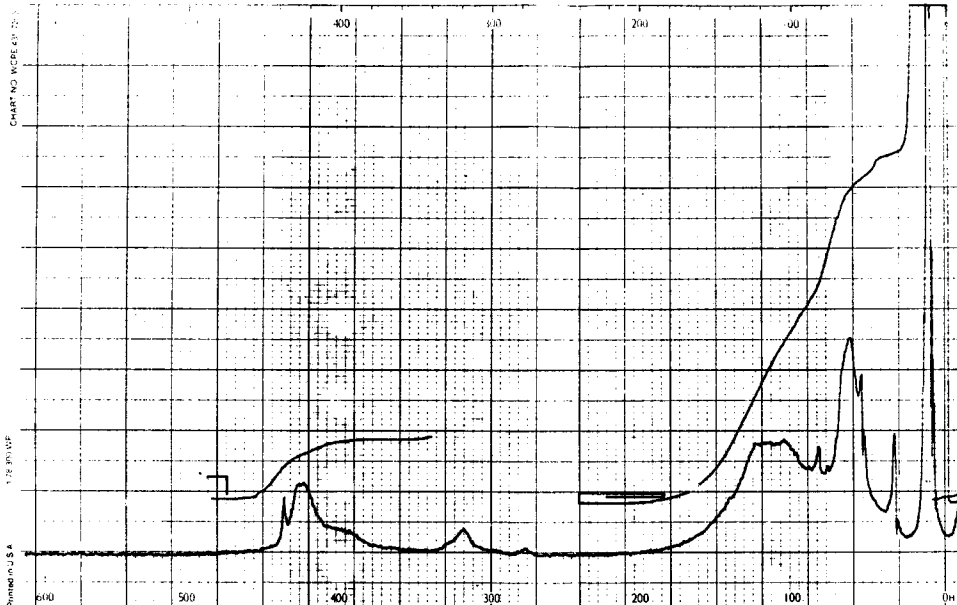
NMR RECORDINGS

styrene





WILMER GLASS CO. INC.  
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601

TMS  
CCL4

9

5

AMPLITUDE  
SPECTRUM  
INTEGRAL

PH LEVEL

PH LEVEL

GAIN

SWEEP WIDTH

FILTER Hz

SWEEP TIME

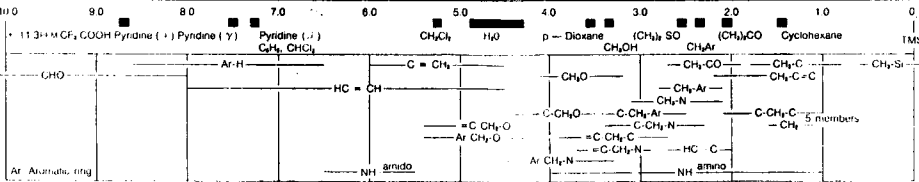
1000 (1000 Hz)

DATE

OPERATOR

G.P.

REMARKS



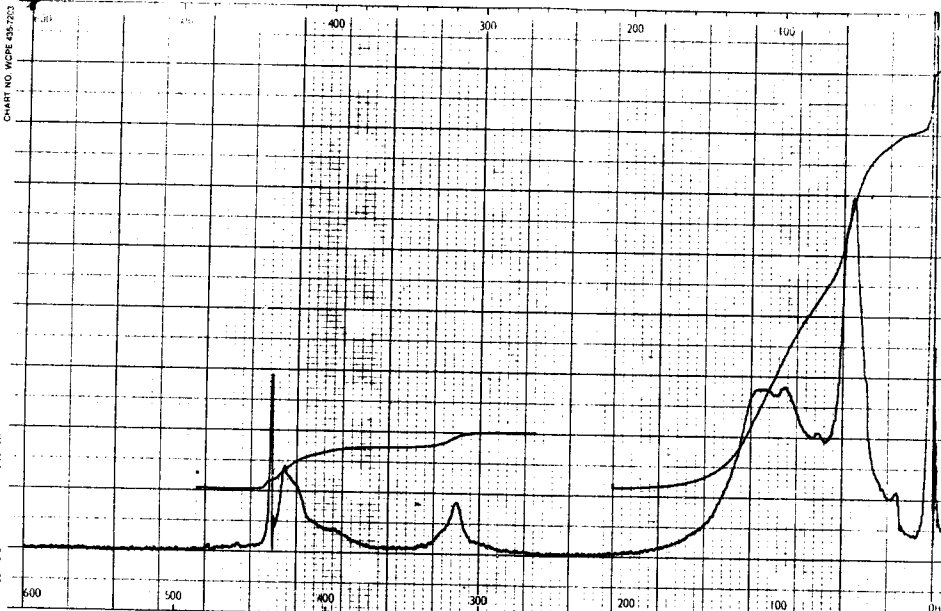
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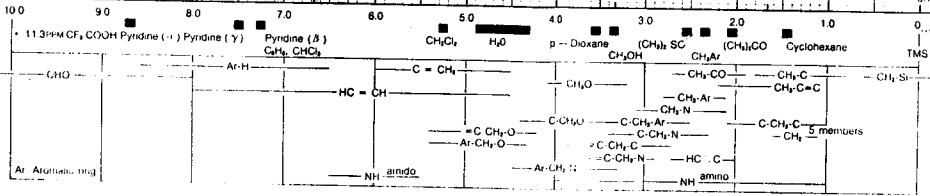
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P. H. M. ADAMS CO. INC.  
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Pittsburgh, U.S.A.

12" NIP



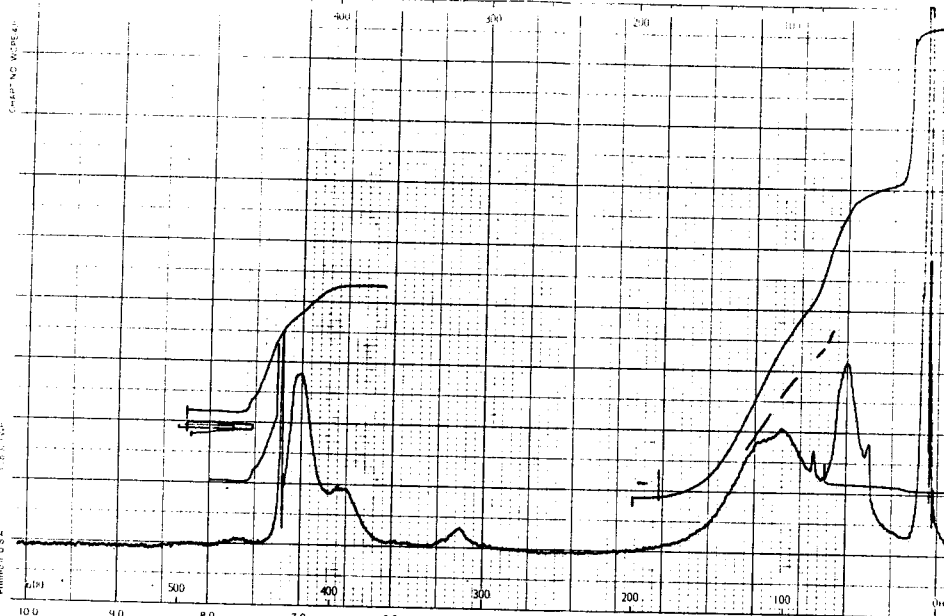
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CONC. *9*  
AMPLITUDE *4*  
SPECTRUM  
INTEGRAL  
HY LEVEL  
HY LEVEL  
GAIN  
SWEEP WIDTH  
FILTER Hz  
SWEEP TIME  
AT 300-150 SEC  
DATE *5/18*  
OPERATOR *G. Park*



REMARKS

(54)

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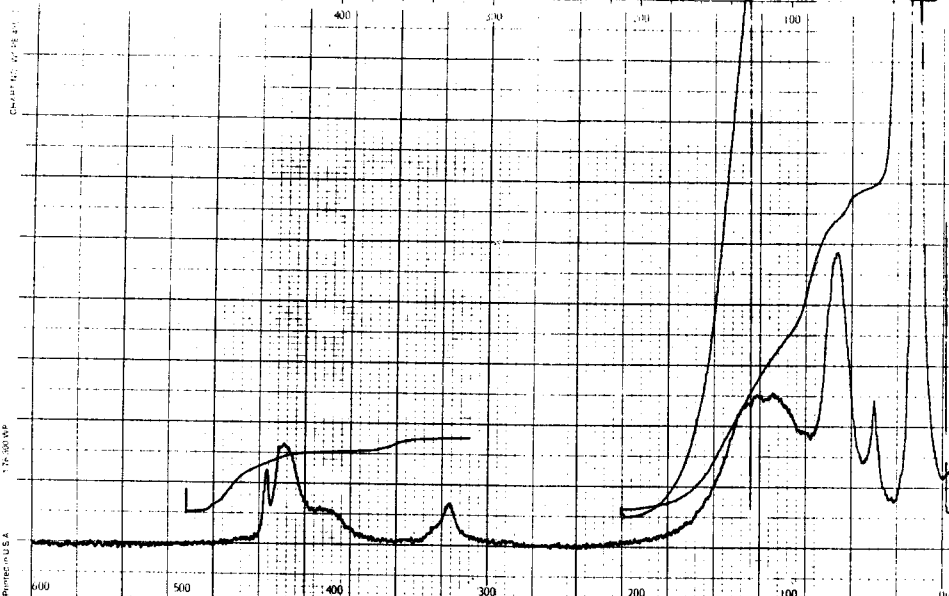


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 CONCN 9  
 AMPLITUDE 5  
 SPECTRUM  
 INTEGRAL  
 PH LEVEL  
 PH LEVEL  
 GAIN  
 SWEEP WIDTH  
 FILTER H<sub>2</sub>  
 SWEEP TIME  
 300-1500 C/P  
 DATE 5-16  
 OPERATOR GP

11.3-10.0 CCl <sub>4</sub> CCl <sub>4</sub> Pyridine (γ)	Pyridine (β)	CH <sub>2</sub> Cl	H <sub>2</sub> O	p-Dioxane	(CH <sub>3</sub> ) <sub>2</sub> SO	CH <sub>3</sub> Ar	(CH <sub>3</sub> ) <sub>2</sub> CO	Cyclohexane	TMS
CHO	Ar-H	HC=CH	C=CH <sub>2</sub>	CH <sub>3</sub> O	CH <sub>3</sub> CO	CH <sub>2</sub> Ar	CH <sub>2</sub> C	CH <sub>2</sub> Si	
Ar: Aromatic ring				C-CH <sub>2</sub> O	C-CH <sub>2</sub> Ar	CH <sub>2</sub> N	CH <sub>2</sub> C=C		
				Ar-CH <sub>2</sub> O	C-CH <sub>2</sub> N	C-CH <sub>2</sub> C	CH <sub>2</sub> 5 members		
				Ar-CH <sub>2</sub> N	HC C	NH amine			
				NH amide					

(47)

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 Buena Vista, N.J. 08181 U.S.A.  
 Printed in U.S.A.



1601

TMS  
 COCl  
 10

REFERENCE  
 SOLVENT  
 GAIN  
 AMPLITUDE  
 GATE TIME  
 INTERNAL  
 PH. LEVEL  
 PH. LEVEL  
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 SWEEP WIDTH  
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 SENSITIVITY  
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 OPERATOR  
 REMARKS

5122

G. P. Park

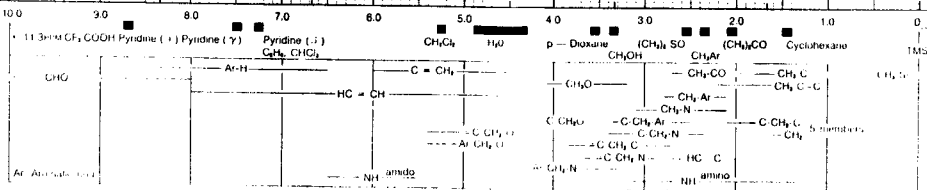
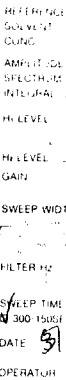


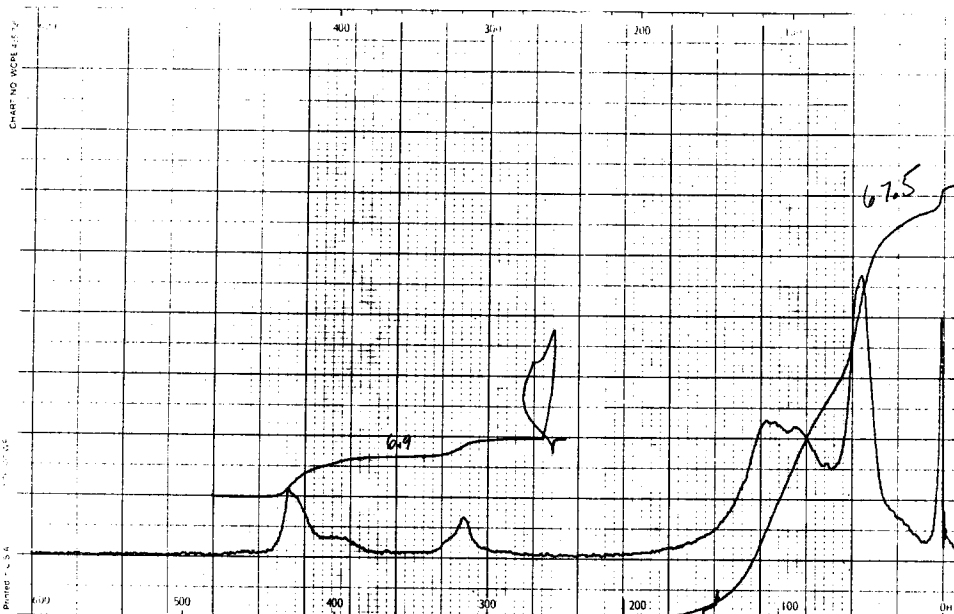
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7

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(64)



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SOLVENT TMS

CONC

9

SPECTRUM

INTEGRA. - - 5

1

H. LEVEL --- -- .

1. *Journal of the American Medical Association*, 1997; 278: 1039-1044.

H<sub>2</sub> LEVEL . . . . .GAIN 2

2.

SWEEP WIDTH .

1. *Introduction*

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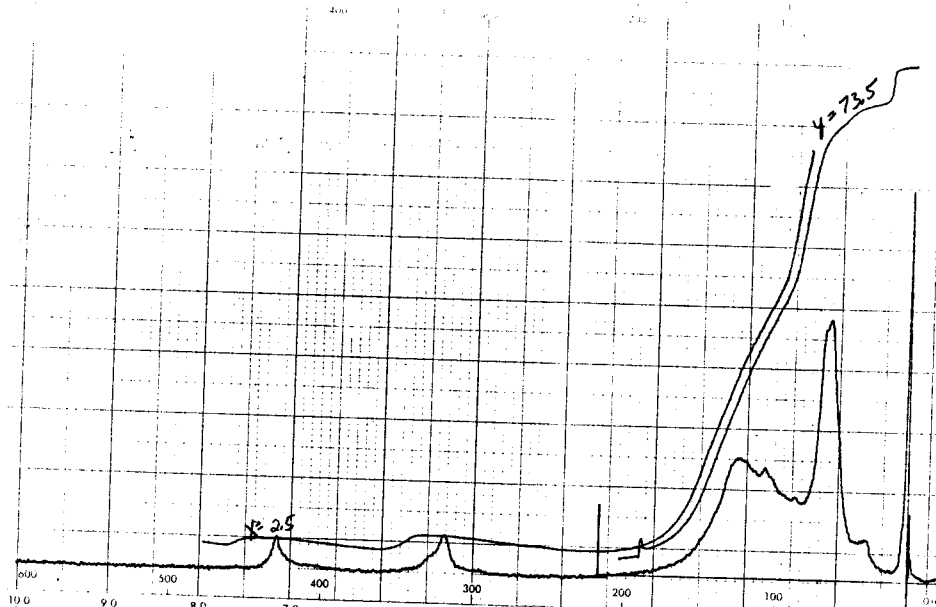
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(50)









702

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CON.

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SPECTRUM 6  
INTEGRAL

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H<sub>2</sub> LEVEL

GAIN

SWEEP WIDTH

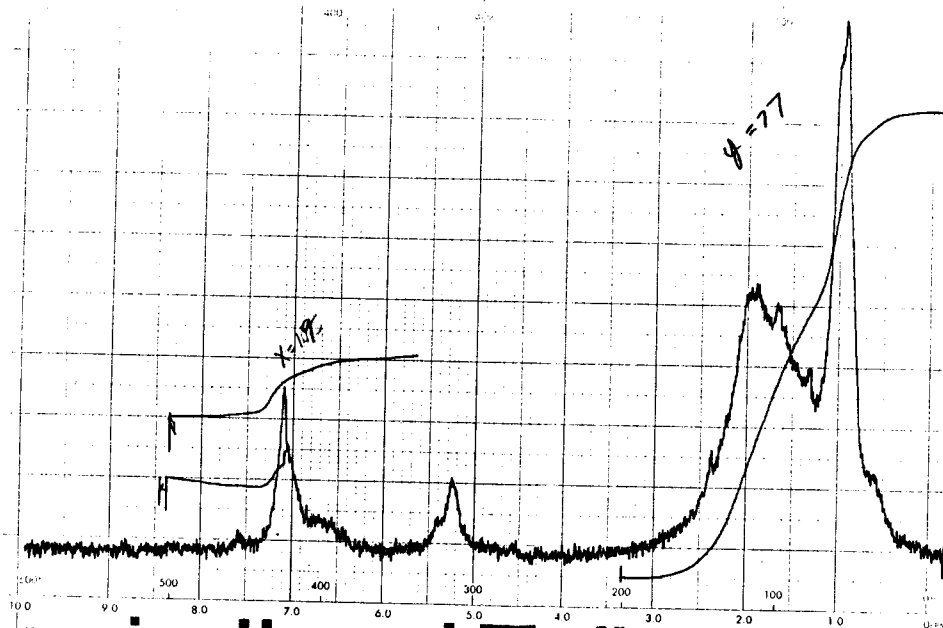
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SWEEP TIME  
☒ 300 ☐ 150 ☐ 75 SEC

DATE 2/19/45

OPERATOR GYP

11.3	10.0	9.0	8.0	7.0	6.0	5.0	4.0	3.0	2.0	1.0	0.0
CHO	Pyridine $\alpha$	Pyridine $\beta$	Pyridine $\gamma$	CH <sub>2</sub> Cl <sub>2</sub>	H <sub>2</sub> O	p-Dioxane	CH <sub>2</sub> OH	(CH <sub>2</sub> ) <sub>2</sub> SO	(CH <sub>2</sub> ) <sub>2</sub> CO	Cyclohexane	TMS
CHO	A-H	HC=CH	C=CH <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	H <sub>2</sub> O	CH <sub>2</sub> OH	CH <sub>2</sub> OH	CH <sub>2</sub> SO	CH <sub>2</sub> CO	CH <sub>2</sub> C	CH <sub>2</sub> S
CHO	A-H	HC=CH	C=CH <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	H <sub>2</sub> O	CH <sub>2</sub> OH	CH <sub>2</sub> OH	CH <sub>2</sub> SO	CH <sub>2</sub> CO	CH <sub>2</sub> C	CH <sub>2</sub> S
CHO	A-H	HC=CH	C=CH <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	H <sub>2</sub> O	CH <sub>2</sub> OH	CH <sub>2</sub> OH	CH <sub>2</sub> SO	CH <sub>2</sub> CO	CH <sub>2</sub> C	CH <sub>2</sub> S



REFERENCE  
SOLVENT  
CONC  
AMPLITUDE  
SPECTRUM  
INTEGRAL

H<sub>1</sub> LEVEL

H<sub>2</sub> LEVEL  
GAIN

SWEEP WIDTH

FILTER H<sub>1</sub>

SWEEP TIME

100 150 SEC ☐

DATE

OPERATOR

REMARKS

TMS  
CDCl<sub>3</sub>

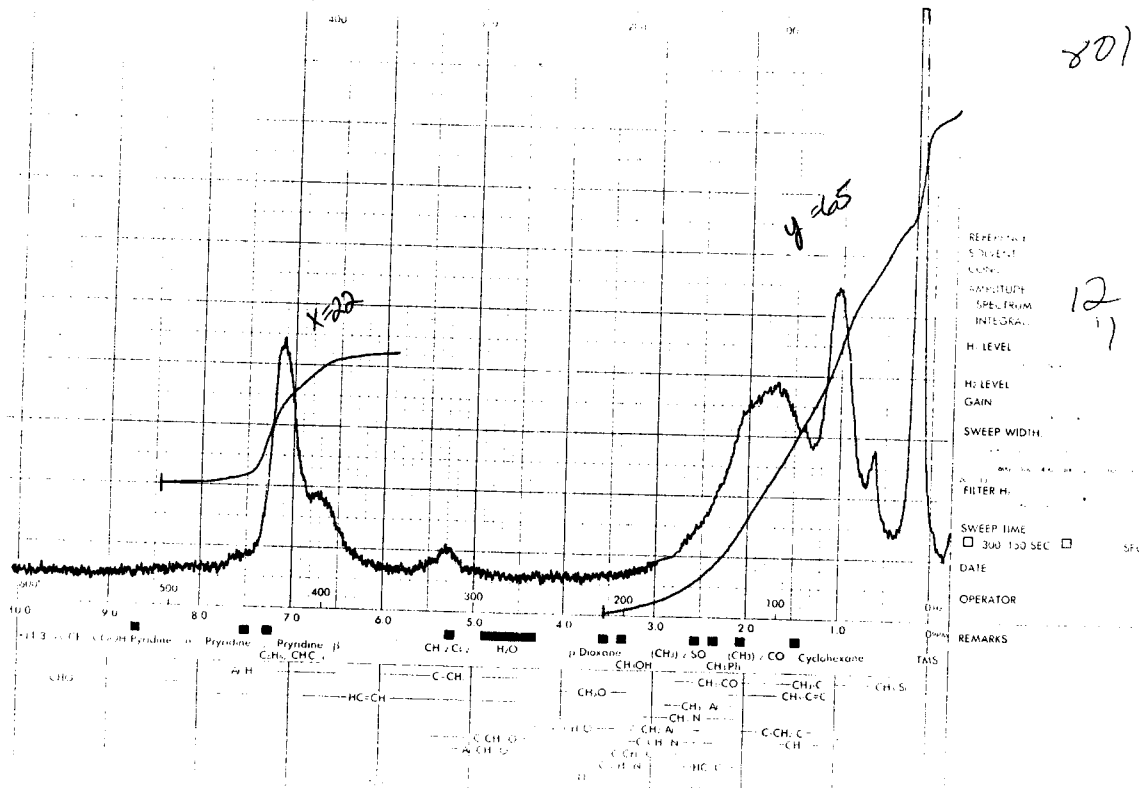
14

703

11.3 ppm CF <sub>3</sub> COOH Pyridine	Pyridine	Pyridine β	CH <sub>2</sub> Cl <sub>2</sub>	H <sub>2</sub> O	p-Dioxane	CH <sub>3</sub> OH	(CH <sub>3</sub> ) <sub>2</sub> SO	CH <sub>3</sub> Ph	(CH <sub>3</sub> ) <sub>2</sub> CO	Cyclohexane	12% S
CH <sub>3</sub>	Ar-H	CH <sub>2</sub> , CH <sub>3</sub>	C=CH <sub>2</sub>	HC=CH	CH <sub>3</sub> O	CH <sub>3</sub> CO	CH <sub>3</sub> Ar	CH <sub>3</sub> C	CH <sub>3</sub> C	CH <sub>3</sub> C	CH <sub>3</sub> C
					H <sub>2</sub> O	CH <sub>3</sub> Ar	CH <sub>3</sub> N	CH <sub>3</sub> C	CH <sub>3</sub> C	CH <sub>3</sub> C	CH <sub>3</sub> C
					CH <sub>3</sub> C	CH <sub>3</sub> N	CH <sub>3</sub> C	CH <sub>3</sub> C	CH <sub>3</sub> C	CH <sub>3</sub> C	CH <sub>3</sub> C
					CH <sub>3</sub> C	CH <sub>3</sub> N	CH <sub>3</sub> C	CH <sub>3</sub> C	CH <sub>3</sub> C	CH <sub>3</sub> C	CH <sub>3</sub> C





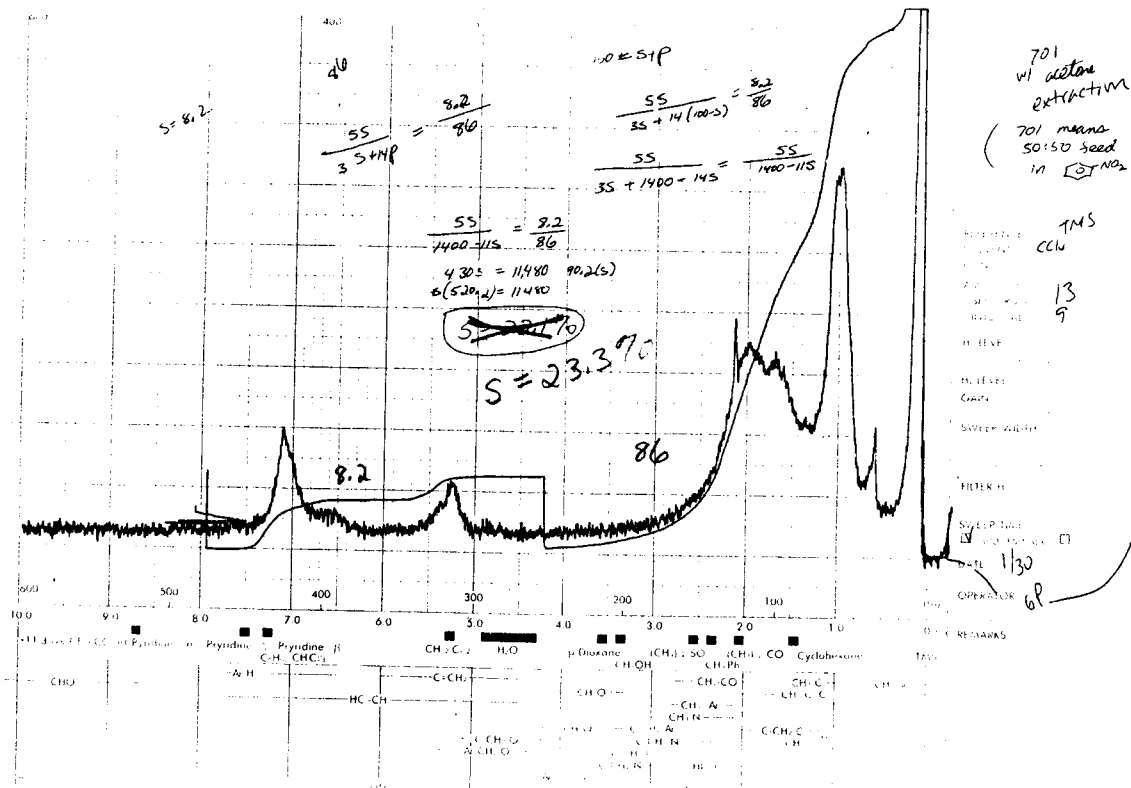












# BIBLIOGRAPHY

1. J. P. Kennedy, Cationic Polymerization of Olefins: A Critical Inventory, Wiley (New York, 1975), pp. 7- 23, 215- 219.
2. R.H. Boundy and R.F. Boyer, eds., Styrene, Reinhold (New York, 1952), pp. 186, 252-253.
3. E.R. Ruckel, H.G. Arlt, Jr. and R.T. Wojik, Polymer Science and Technology, 9A, 395 (1975).
4. J.P. Kennedy and T. Chou, Advances in Polymer Science, 21, 1 (1975).
5. H. Pietila, A. Sivola and H. Sheffer, J. of Poly. Sci., 8, 727 (1970).
6. A. Sivola and C. Harva, Somen Kemistilehti B, 43, 475 (1970).
7. C. Snyder, W. McIver and H. Sheffer, J. of Applied Poly. Sci., 21, 131 (1977).
8. H. Sheffer, A. Sivola and J. Savelainen, Finn. Chem. Letters, 122 (1978).
9. R.B. Seymour, Introduction to Polymer Chemistry, McGraw- Hill (New York, 1971), pp. 168-192.
10. P.J. Flory, Principles of Polymer Chemistry, Cornell University Press (New York, 1953), pp. 218- 260.
11. D.B. Parker, Polymer Chemistry, Applied Science Publishers (London, 1974), pp. 103- 118.
12. G.E. Ham, Vinyl Polymerization, Part II, Marcel Dekker (New York, 1969), pp.231- 282.
13. C.E. Schildknecht, ed., Polymerization Processes, Wiley (New York, 1977), p. 312.
14. G. Odian, Principles of Polymerization, Wiley (New York, 1970), pp. 365- 371, 472- 476.
15. T. Kelen and F. Tudos, J. Macromolecular Sci.- Chem., A9(1), 1(1975).
16. J.P. Kennedy, T. Kelen and F. Tudos, J. Poly. Sci., 13, 2277(1975).
17. T. Kelen, F. Tudos, J.P. Kennedy and B. Turcsanyi, J. Poly. Sci., 15, 3047 (1977).
18. C.G. Overberger and V.G. Kamath, J. Am. Chem. Soc., 81 2910 (1959)

19. P. Lebel, Rubber and Plastics Age, (June, 1965), pp. 677, 681-682.
20. C.P. Smyth, Dielectric Behavior and Structure, McGraw- Hill (New York, 1955), pp. 1, 17, 257- 258, 316.

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