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Four additional batches of polyethylene (PE)-supported palladium catalyst were prepared. These catalysts have been evaluated for the preparation of a diynol addition product 2 starting from 4,4'-bis(3-bromophenoxy) diphenyl sulfone 1 (Figure 1). Palladium still leaches into the product. The reaction conditions of palladium complexation with triphenyl phosphine (TPP) were studied. The optimum amount of TPP required in the diynol addition reaction was lowered to a range of one-half as compared to the established procedures. Under the Biotech-Support part of this program, reaction conditions favoring condensation of phenols and aromatic halides were explored using model reactions of m-cresol and dichlorodiphenyl sulfone and difluorobenzophenone. Condensation reactions were faster in the presence of 18-Crown-6 than CsI. Difluorobenzophenone reacted faster than dichlorodiphenyl sulfone with m-cresol. The reaction conditions were applied to the condensation of m-hydroxyphenyl acetylene and aromatic dihalides.

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AT-RESIN RESEARCH: BIOTECHNICAL SUPPORT AND HETEROGENEOUS CATALYSIS

~~Interim~~ Technical Report

September 1, 1989 to July 15, 1990

AT-RESIN RESEARCH: BIOTECHNICAL SUPPORT AND HETEROGENEOUS CATALYSIS

Contract #: FQ8671-8900317

Subject: ~~INTERIM~~ TECHNICAL REPORT

For period covering September 1, 1989 to July 15, 1990

Contract for :
Air Force Office of Scientific Research
Bolling Air Force Base, DC 20332-6448

Work performed by:
Dexter Adhesives & Structural Materials Division
Hysol Aerospace, Inc.
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Report written by:
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1.0 SUMMARY

Work on Task I and II of the contract was continued during the period September 1, 1989 to July 15, 1990.

Four additional batches of polyethylene (PE)-supported palladium catalyst were prepared by Penn State University. These catalysts have been evaluated for the preparation of a diynol addition product 2 starting from 4,4'-bis(3-bromophenoxy) diphenyl sulfone 1 (Figure 1). Palladium still leaches into the product. The reaction conditions of palladium complexation with triphenyl phosphine (TPP) were studied. The optimum amount of TPP required in the diynol addition reaction was lowered to a range of one-half as compared to the established procedures published by the Air Force Material Laboratories and Dexter Hysol.

Under the Biotech-Support part of this program, reaction conditions favoring condensation of phenols and aromatic halides were explored using model reactions of m-cresol and dichlorodiphenyl sulfone and difluorobenzophenone. Condensation reactions were faster in the presence of 18-Crown-6 than CsI. Difluorobenzophenone reacted faster than dichlorodiphenyl sulfone with m-cresol. The reaction conditions were employed to the condensation of m-hydroxyphenyl acetylene and aromatic dihalides.

2.0 PROGRAM OBJECTIVES

The program contains the following objectives for this period:

1. Continue the development (preparation) work on the polyethylene (PE)-supported palladium catalyst.

2. Evaluate the performance of the catalyst in the reaction of 4,4'-bis(3-bromophenoxy) diphenyl sulfone (Ullmann product) and 2-methyl-3-butyn-2-ol (butynol) to generate a blocked

acetylene terminated (AT) resin. Propose a plausible mechanism for the above reaction.

3. Optimize the amount of triphenyl phosphine (TPP) in the reaction of Ullmann product and butynol.

4. Study the hydrolysis reaction of m-hydroxyphenyl acetylene-tosylate salt followed by its condensation with dichlorodiphenyl sulfone and difluorobenzophenone.

5. Explore catalysts for facilitating the condensation of m-hydroxyphenyl acetylene and aromatic dihalides.

3.0 BACKGROUND

Acetylene terminated resins constitute an important class of easily processible high performance thermosetting resins which may be useful in many applications, including, for example, high temperature composites, adhesives, and electrical insulation. Among the principle advantages of these resins is that they do not produce volatiles upon curing, thus eliminating voids within the material products.

A significant disadvantage of AT resins is their relatively high manufacturing cost. Much of this cost is attributable to the end-capping of α ω-dibromoarenes (Ullmann product) with acetone-blocked acetylene using a palladium catalyst. Specifically, the problem lies with both an expensive catalyst removal process and an inability to recover the catalyst so that it can be used again.

In order to alleviate the above problems, binding the palladium catalyst onto a polyethylene-support was proposed. This should allow for a simplified and inexpensive catalyst removal by filtration at the end of the reaction. Furthermore, the

recovered catalyst should be reusable. In a published report by marvel and Trumbo[1], the polyethylene supported palladium catalyst was demonstrated to be both easily separated from the reaction products and reusable without a significant loss of catalytic activity.

A few additional batches of polyethylene supported palladium catalyst were prepared and evaluated for performance of its utility in the synthesis of AT resins. A discussion of catalyst leeching and our approaches to solve this frustrating problem has been addressed.

The other approach for generating the AT resins through a reaction of m-hydroxyphenyl acetylene with activated aromatic dihalides is potentially inexpensive. Current AFOSR research into low cost biotechnical routes to m-hydroxyphenyl acetylene (BTR-Meeting update, June 1990) and its precursor, phenyl-acetylene, has shown a considerable success. However, research into the reaction between m-hydroxyphenylacetylene and dichlorodiphenylsulfone, to yield the desired acetylene terminated resin, is critical to the success of this overall program. Basic work by the Air Force Materials Lab has shown this reaction to be very sluggish and uneconomic. This condensation reaction has also been attempted under different conditions.

4.0 RESEARCH & DEVELOPMENT STATUS REPORT

4.1 Preparation of Polyethylene (PE)-Supported Catalyst

The research work on the preparation of PE-supported palladium catalyst was done at Penn State University. Additional batches of the catalyst were prepared following Marvel's and modified procedures. The synthesis of the catalyst involves the following three major steps and several substeps.

4.1.1 Preparation of Polyethylene Single Crystals

1.0 g Polyethlene (PE)[2] was dissolved in one liter of refluxing anhydrous (distilled over benzophenone ketyl) xylene. The homogeneous solution was heated in a 102°C oil bath for two hours, after which it was transferred to another 88°C oil bath and stabilized for 8 hours. During this time, single PE crystals were formed.

The solution was removed from the oil bath and allowed to cool down to room temperature slowly. The crystals were filtered through a glass frit and washed with CCl_4 and dried.

4.1.2 Bromination of Polyethylene Single Crystals

6.0 g bromine was dissolved in 250 mL CCl_4, forming a bright red homogeneous solution. 2.0 g of the single crystals were added to the solution and the heterogeneous mixture was transferred to the photochemical reactor.[3)] The suspended crystals were added to the solution and the heterogeneous mixture were irradiated for 1.5-2 hours under a steady stream of nitrogen. The solution was then filtered and the polyethylene was thoroughly washed with CCl_4 and then THF.

Approximately 5 mg of the product was dried and sent to The Brazeal Nuclear Reactor at Penn State for bromine analysis. The results of these analyses are given in Table 1.

Table 1

Weight-Percent Bromine in PE-Br Samples[a]

no.[b]	wt.-%	no.[b]	wt.-%
1	2.29	4C	5.76
2	1.86	**8****	16.4
3	14.5	**9****	13.8
4	20.0	10	5.91
3B*	4.13	**11****	23.0
4B	0.91	**12****	18.6
27	3.03	13	5.14
56*	4.90	27B	7.57

[a] Analyzed at Brazeal Nuclear Reactor at Penn State. [b] Bold print denotes sample of the final catalysts prepared from PE-Br ultimately evaluated at Dexter Hysol. Samples having equal numbers of asterisks were eventually combined in the phosphination procedure.

4.1.3 Phosphination of Single Crystals

0.5 g of lithium powder was added to 150 mL dry THF. The suspension was cooled to 0°C and 13 mL $ClPPh_2$ was added slowly over a period of 30 minutes. The solution was warmed to room temperature and allowed to stir for an additional 6 hours. The resulting heterogeneous solution was filtered to yield a red filtrate.

2.0 g brominated polyethylene single crystals were then added to the red $LiPPh_2$ solution. The heterogeneous solution was stirred for two days at room temperature before heating to reflux for an additional day. A heterogeneous mustard-yellow colored solution was formed, which was cooled to room temperature.

The phosphinated single crystals were finally isolated by filtration. They were washed with THF, H_2O, THF, and CH_2Cl_2.

Approximately 50 mg of each sample was sent to Galbraith Laboratories for phosphorous analysis.

4.1.4 Palladation of Single Crystals

Thus far, two different palladium catalysts have been bound to polyethylene single crystals. The experimental procedures are described below. P and Pd analyses were performed by Galbraith Laboratories.

1. Preparation of PE-PPh_2--$\overset{Cl}{\underset{Cl}{Pd}}$--NCPh

0.250 g $(PhCN)_2PdCl_2$, prepared according to the method of Kharasch, was added to 2.0 g phosphinated polyethylene single crystals in CH_2Cl_2. The heterogeneous solution was allowed to stir at room temperature for 1 hour. The mixture was filtered and the light brown polyethylene single crystals were washed with CH_2Cl_2 until the filtrate was consistently colorless.

2. Preparation of PE-PPh_2--$\overset{Cl}{\underset{Cl}{Pd}}$--$PPh_3$

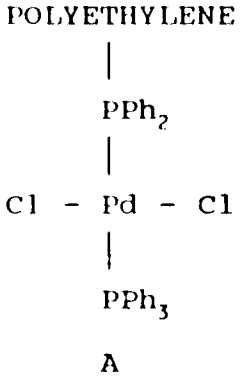
a. Benzonitrile Substitution using $(PhCN)_2PdCl_2$

To the light brown crystals prepared in #1 above were added 0.250 g PPh_3. The mixture was allowed to stir for 0.5 hour at room temperature, after which time it was filtered. The yellowish precipitate was washed with CH_2Cl_2 until the filtrate was consistently colorless.

b. Phosphine Equilibration using $(PPh_3)_2PdCl_2$

The procedure described is basically that of Trumbo and Marvel.[1] 2.0 g of phosphinated single crystals were suspended in 250 ml toluene. To this mixture was added 2.0 g $(Ph_3P)_2PdCl_2$. The heterogeneous mixture was allowed to stir at room temperature for 17 days before being filtered and washed with toluene. The crystals were stirred in toluene overnight and filtered again.

This procedure was repeated until the filtrate came through perfectly colorless--approximately 6 times.



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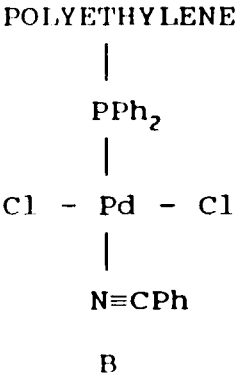


B

Catalyst Sample #1

The brominated polyethylene single crystals are labelled #3 (14.5 wt.-% Br) in Table 1. The polymer was phosphinated as described above, but was not analyzed for phosphorous content before being palladated. The method of palladation was described above as procedure 2a, forming catalyst A. This sample was evaluated at Dexter Hysol, which sent a portion to Galbraith Labs for P and Pd analyses (Pd analysis revealed 3.8 wt.-%).
Evaluation results of this catalyst were included in the First Interm Report.

Catalyst Samples #2,3,4

Brominated samples #3B (4.13 wt.-%) and #56 (4.90 wt.-%) were combined. The mixture (4.52 avg. wt.-% Br) was phosphinated as described. Galbraith analysis indicated 0.51 wt.-% phosphorous. The phosphinated single crystals were divided into approximately three equal portions and palladated as follows.

Catalyst Sample #2

Procedure 1 was used to generate catalyst B. Galbraith analysis indicated 0.48 wt.-% phosphorous and 4.87 wt.-% Pd.

Catalyst Sample #3

Procedure 2a was used to generate catalyst A. Galbraith analysis indicated 0.58 wt.-% phosphorous and 0.67 wt.-% Pd.

Catalyst Sample #4

Procedure 2b was used to generate catalyst A. Galbraith analysis indicated 0.58 wt.-% phosphorous and 0.67 wt.-% Pd.

Catalyst Sample #5

Brominated batches #8, #9, #11, and #12 were combined. The mixture (17.9 avg. wt.-% Br) was phosphinated according to the above procedure. The crystals were then palladated according to procedure 2b to generate catalyst A. Palladium analyses from Galbraith Laboratories revealed 1.9 and 2.86%, respectively. This sample is currently being evaluated at Dexter-Hysol.

5.0 Evaluation of the Catalyst

Catalyst Sample #1

During the evaluation, this sample lost about 80% of palladium. Results of this experiment were included in the First Interim Report submitted in October 1989.

Catalyst Sample #2

This sample also lost more than 80% palladium during first use in the diynol synthesis (Table 2).

Table 2: Palladium Concentration Before and After the First Use

Palladium Concentration Before Rxn %	After Rxn	Reaction Time(Conversion),h 50%	100%	Pd Contamination in Prod., ppm
4.87	0.51	7.5	18	76

The palladium concentration left in the catalyst, after the first

use, was so low that it could not be recycled. The palladium contamination of the product was much higher than the Air Force specifications. The concentrations of individual reactants and intermediates are given in Figure 2.

Catalyst Sample #3

This sample lost about 60% of palladium after the first use. Upon recycling, it lost about 30% additional palladium. For some unknown reasons, the recycling experiment took about 2/3 less time for completion as compared to the first experiment (Table 3).

Table 3: Palladium Concentration Before and After the First and Second Use

Cycle #	Pd Conc. in Catalyst,% Before RXN	After RXN	Reaction Time, h 50% Conv.	100%	Pd in Prod. ppm
1	1.61	0.63	12	24	290
2	0.63	0.42	1.5	9.5	43

The diynol addition product was quite contaminated (290 ppm) with Pd during the first reaction which dropped to 43 ppm in the second reaction. The rate of reaction and the concentration of individual components (based on the HPLC analysis of the reaction mixture at a given time) is given in Figure 3.

Catalyst Sample #4

The catalyst sample #4 originally had a low level (0.67) of Pd. After the first use the Pd concentration dropped down to 0.13% (Table 4). The Pd concentration was very low and the catalyst could not be recycled.

Table 4: Palladium Concentration Before And After First Use

Palladium Concentration Before Rxn	After Rxn	Reaction Time(Conversion),h 50%	100%	Pd contamination in Prod., ppm
%				
0.67	0.13	2.5	12	29

The Pd contamination of the product was much lower than the other experiments.

The evaluation results for all the above batches of the catalysts are summarized in Table 5.

Catalyst Sample #5

The catalyst sample #5 has been evaluated under the same conditions of earlier reactions. The rate of the diynol addition reaction was fast.

Table 6: Palladium Concentration Before and After the First Use

Pd Concentration, % Before Rxn	After Rxn	Time (% Conversion), h 50%	100%	Pd (ppm)in Product
2.86	--	<1	8	--

The catalyst has been recovered and is being analyzed for the residual palladium

So far, the PE-supported catalysts (Sample #1-4) did not show any encouraging results to support the recyclability of the catalyst or a strong binding between Pd polyethylene. A plausible mechanism of the transformation revealed some interesting characteristics which might be responsible for the lower performance of the catalyst. Any additional components such as, TPP concentrations, which might contribute to enhance the reaction rate were also investigated.

6.0 Effect of TPP and TPP Concentration on the Diynol Addition Reaction

During the evaluation of catalyst sample #5, the presence of TPP in the diynol addition reaction was rationalized by reviewing all the steps involved in the mechanism. The effect of TPP concentration was also studied. Two reactions, conducted in absence of TPP, showed no reaction which indicated that the reaction requires TPP. The optimization of TPP concentration in the reaction was attempted by conducting the reaction in the presence of varying amount of TPP. The optimization of TPP was thought as critical to minimize Pd leaching from the catalyst. The active species generated from the PE-supported-Pd catalyst would prefer to bind with free TPP than the polymer-supported-TPP, thereby, making the new active catalyst soluble and increasing the possibility of Pd leaching.

In the past, the amount of TPP used in the diynol addition reaction with the conventional bis-TPP-Pd(II) chloride catalyst was taken as a standard (full amount) for all previous evaluations. Four reactions, using 1/2, 1/4, 1/8 the standard amount of TPP along with catalyst sample #5 were conducted. Reaction containing 1/8 and 1/4 of TPP were very slow while the reaction containing 1/2 TPP proceeded well during the first set of reactions. But when the latter reaction (containing 1/2 of standard TPP) was repeated, the rate was found slower than the full amount.

The rate of diynol addition reaction in the presence of 1/2 vs. full amount of TPP is compared in Table 7. In the subsequent evaluations, a full amount of TPP will be used in the diynol addition reactions.

Table 7: Comparison of Diynol Addition Reaction in the Presence of Full and 1/2 TPP

TPP	Pd Conc. in Catalyst, % Before RXN	After RXN	Reaction Time, h 50% Conv.	100%	Pd in Prod. ppm
Full	2.86	---*	1	8	---*
Half	2.86	0.96	1	24	35

* Analysis results are not yet available.

The reaction which contained half the amount of TPP was slower after the consumption of 50% of the Ullmann product. The concentration of individual components, of these two reactions are compared in Figure 4.

7.0 Mechanism of Diynol Addition Reaction

Marvel and Trumbo reported the synthesis of bis(phosphine) palladium chloride supported on polyethylene single crystals.[1)] This heterogeneous catalyst was further reported to be effective in catalyzing the reaction of aryl halides with terminal acetylenes. Furthermore, they claimed the catalyst to be reusable, with only a small loss of catalytic activity and virtually no leaching of palladium from its support. The diynol addition reactions were conducted int he presence of TPP.

Attempts to repeat the results of Marvel and Trumbo at Dexter Hysol was unsuccessful. In our studies, it was observed that the catalyst leaches off the polymer support, thus contaminating the reaction products and rendering the catalyst useless for subsequent reactions. The catalyst activity went on decreasing after each use and the reaction rate, at same Pd concentration, was similar to the regular $[(TPP)_2PdCl_2]$ catalyst. The cause of this apparent discrepancy has not yet been fully determined, although both the method of catalyst preparation and the

experimental procedure used during catalysis might have greatly affected the results.

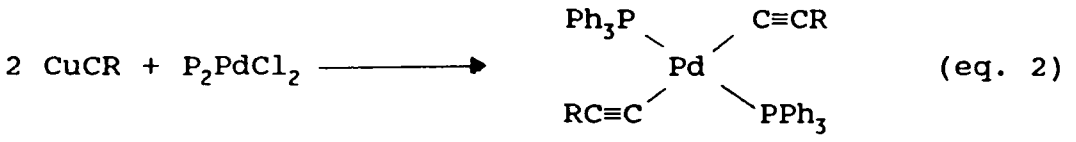
There are several steric and electronic features of supported catalysts which may make them more or less likely to leech from the polymer support. It is necessary to identify and understand these features if one is to redesign a supported catalyst or to understand its shortcomings. In order to evaluate these catalysts it is necessary to understand both the mechanism of the reaction which is catalyzed and all the possible side-reactions which the catalysts may undergo during the course of catalysis, especially if a side reaction will render the catalyst inactive or cause it to leach from the polymer support. Thus, the following discussion centers on the organometallic chemistry associated with the catalytic process. It should be noted that there are several processes which could ultimately result in catalyst leaching.

Although the mechanism of the palladium-catalyzed coupling of aryl halides and terminal acetylenes has not been unequivocally established, a very logical mechanism has been proposed as Schemes 1 and 2.[4] Scheme 1 represents the formation of the actual catalyst from the precursor complex. Scheme 2 then demonstrates the mechanism of product formation during the catalytic cycle.

The process begins with the reaction of cuprous halide and a base with a terminal acetylene to generate a cuprous acetylide (eq. 1). Two equivalents of cuprous acetylide then react with the

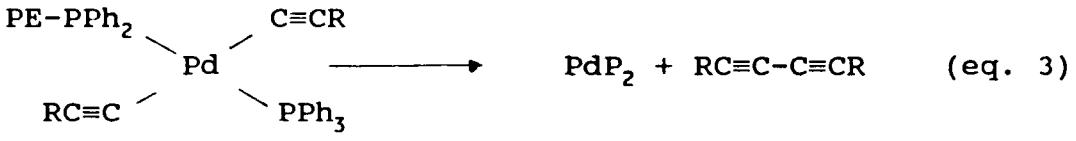
$$CuX + HC{\equiv}CR \xrightarrow[-\ HNEt_3X]{+\ NEt_3} CuC{\equiv}CR \qquad \text{(eq. 1)}$$

bis-(phosphine) palladium (II) chloride via metatheses to regenerate cuprous halide and to form a bis(phosphine)diacetylide palladium (II) complex (eq. 2). This complex then undergoes a



(eq. 2)

reductive elimination of the acetylides (eq. 3) to form an organic product and bis(phosphine) palladium (0).

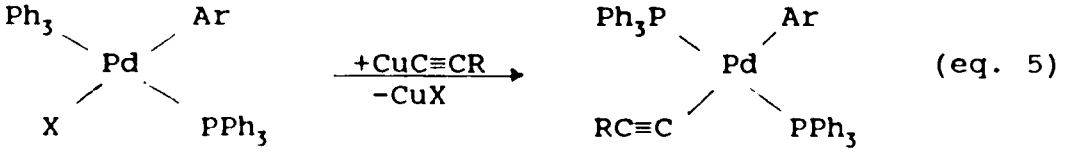


(eq. 3)

The above process generates the "true" catalyst in the coupling reaction -- $P_2Pd(0)$. In the catalytic cycle, P_2Pd (0) reacts with an aryl halide via oxidative addition to form a bis(phosphine)(aryl)(halide)palladium (II) complex (eq. 4), which

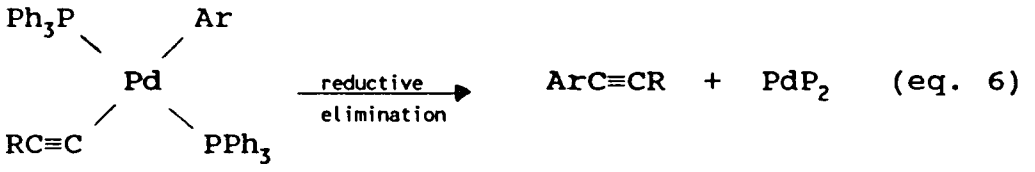
(eq. 4)

subsequently undergoes metathesis with cuprous acetylide to generate a new palladium (II) species having bonds to an aryl group and a terminal acetylene in addition to the two phosphine ligands (eq. 5). Finally, the organic ligands are coupled via



(eq. 5)

reductive elimination (eq. 6) to form the desired organic product and to regenerate the catalyst -- P_2Pd (0). This completes one catalytic cycle while initiating another. It is important to note here that the recovered catalyst is NOT that which was initially used. After one cycle, the catalyst will never exist as Pe-supported-palladium catalyst.



The above mechanism is actually quite simplified from the overall process. Each step in Scheme 2 can be further broken down into a series of steps, each encompassing entirely different intermediates. Thus trying to determine the exact cause of palladium leaching is rather difficult process.

Furthermore, the addition reaction does not proceed without TPP. The active form of the catalyst as shown in Equation 2 may be different than PdP_2(Di-complex). The formation of PdP_4(Tetra-complex), in palladium-catalyzed reactions, has been mentioned in several recent papers[5]. The formation of a Tetra-complex can occur during the diynol addition reaction only in the presence of an excess amount of TPP. The exact amount of TPP required to produce the stable Tetra-complex has not been determined but it appears that excess TPP favors its formation. Additionally, The reaction only proceeding in presence of TPP indicates that this complex might be forming during the reaction and also might be responsible for the reaction. In addition to the formation of this complex, there may be some side reactions, irreversible cleavage polymer-phosphorous bonds, might be occurring. Such side reactions can generate a soluble catalyst which might be causing the leeching problems. These cleavage reactions may also be dependent on the solvent which has not been studied in detail.

Penn State is working on improving upon the leaching problem by binding active palladium to a polymer via a chelating phosphine ligand. Since the chelating ligands are not readily dissociated from metal complexes, it is anticipated that leeching will be minimized. Furthermore, the chelating ligands should impart additional stability to metal, thus preventing premature deactivation via side reactions.

9.0 Reaction of Hydroxyphenyl Acetylene and Aromatic Dihalides

A significant progress to investigate the reaction conditions for condensing m-hydroxyphenyl acetylene (m-HPA) and aromatic dihalides was made. The m-HPA is expensive. A similar phenol, m-cresol as a model, for such condensation reactions was suggested by Dr. Hedberg. A few reactions were tried with m-cresol and optimization of condensation reaction was established by HPLC methods. Several catalysts, such as cesium iodide, 18-crown-6 etc., were tried. A few mixtures of NMP (N-methylpyrrolidinone) and toluene were used as a solvent.

9.1 Reaction of m-Cresol and Dichlorodiphenyl Sulfone and Difluorobenzophenone, using CsI as a Catalyst

Using potassium salt of m-cresol and the dihalide in the ratio 2:1, the reaction was carried out in 8% NMP in toluene. Cesium iodide was used as a catalyst. The reaction temperature averaged to 117°C. The reaction of difluorobenzophenone was faster than dichlorodiphenyl sulfone. The diflurobenzophenone reaction was still slow and even after 20 hours only 40% of the condensation product was formed (Figure 5).

The reaction required some additional improvements in the conditions. Since the reaction of difluorobenzophenone was faster than dichlorodiphenyl sulfone, the former was studied in detail. Furthermore, the AT resin from benzophenone has shown

quite interesting properties which are comparable to the ATS (sulfone) resin[6].

9.2 Reaction of m-Cresol and Difluorobenzophenone using 18-Crown-6 as a Catalyst

A reaction of 2 moles of potassium salt of m-cresol and 1 mole of 4,4'-difluorobenzophenone, using toluene:NMP (100:20) solvent mixture and 18-crown-6 as a catalyst, was carried out. This catalyst performed better than CsI. But the reaction took about 35 hours for 95+% completion. The results are included in Figure 6.

9.3 Reaction of m-Hydroxyphenylacetylene (HPA) Tosylate and Difluorobenzophenone using 18-Crown-6 as a Catalyst

The tosylate salt of m-HPA was hydrolyzed and the reaction was carried out under the conditions as mentioned above. AT the initial stage, the reaction was slow (Table 8).

Table 8: Component Concentration (%) in Hydroxy Phenylacetlene and Difluorobenzophenone Reaction:

Elapsed Time, Hours	Starting Materials	Intermediate	Final
0	100	0	0
2[1]	100	0	0
6	39	55	6
10	21	64	15
25	8	60	32
41[2]	2	56	42
47 (post)	2	35	63
55	2	22	76

[1] 18-Crown-6 was added (additional amount).
[2] Tosylate salt and potassium hydroxide added.

An increase in the reaction rate, after the addition of an extra amount of the tosylate salt (after 40 hours) indicated that either the tosylate salt did not completely hydrolyse or some impurities existed in the tosylate salt.

The reaction has been repeated by increasing NMP ratio from 15 to 25 in 100 mL of toluene and using 20% excess of pure m-HPA tosylate. The results are included in Table 9 , which clearly indicates a higher reaction rate as compared to the previous reaction. The reaction temperature was 5-7°C higher than the previous reaction.

Table 9: Component Concentration (%) in Hydroxy Phenylacetlene and Difluorobenzophenone Second Reaction:

Elapsed Time, hours	Starting Materials	Intermediate	Final
0	100	0	0
0.5	61	37	2
1	31	61	8
6	7	70	23
11	7	66	27
17.5	1	43	56
33	1	13	86
49	<1	0	>99

Some of the selected HPLC analysis chromatograms of the rection mixture checked during the reaction are shown in the Figures 7 - 13. The HPLC analysis of the AT resin containing benzophenone (AT-Benzo), prepared by two different methods, is given in Figures 12 and 13, which indicates that both (AT-Benzo resins) are the same.

This reaction is still being studied for optimization of the reactant amounts and reaction temperature.

10.0 Personnel

10.1 Dexter Adhesives & Structural Materials Division (Dexter Hysol, Inc.)

David K. Klapprott	Program Manager
Yesh P. Sachdeva	Principle Investigator
Stewart Williams	Laboratory Technician (Temporary)

10.2 Materials Science Department, Penn State University

Bernard Gordon III	Principle Investigator (Sub-Contractor)
Jeff Brumbaugh	Post-doc Research Associate

11.0 FUTURE WORK

1. Penn State will be working on designing a better ligand for binding palladium to polymers.

2. Dexter Hysol will be evaluating the polymer-supported catalysts prepared by Penn State.

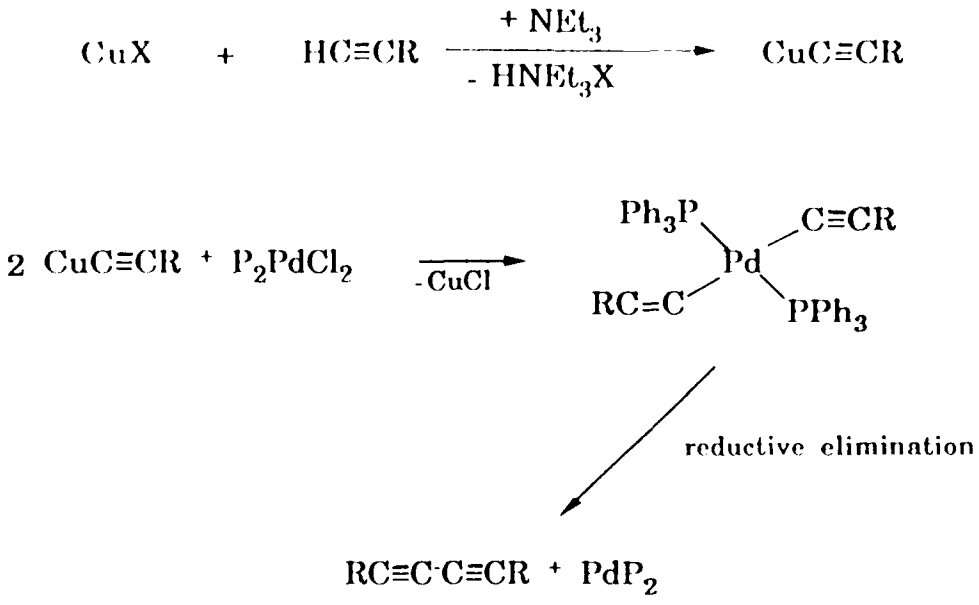
3. Dexter Hysol will be optimizing reaction conditions for condensing m-hydroxyphenyl acetylene and difluoro-benzophenone. One additional attempt will be made to condense m-hydroxyphenyl acetylene with dichlorophenyl sulfone.

4. Evaluation of catalyst sample #5 will be completed during next month.

12.0 References

1. D.L. Trumbo and C.S Marvel, J.Poly.Sci., Poly Symp, 1986, 74, 45.
2. Marlex 6001 high density PE crystallized from xylene.
3. Photochemical reactor from Ace Glass/450 watts lamp.
4. K.A. Horn et. al., J. Organmet. Chem., 1987, 332, 271.
5. D.E. Bergbreiter et. al., J. Org. Chem., 1989, 54, 2726 and references cited there-in.
6. Y.P. Sachdeva et. al., J. Adhesion, 1990 (in press).

Scheme 1. Formation of True Palladium Catalyst from Precursor



Scheme 2. Mechanism of Palladium-Catalyzed Coupling of Aryl Halides with Terminal Acetylenes

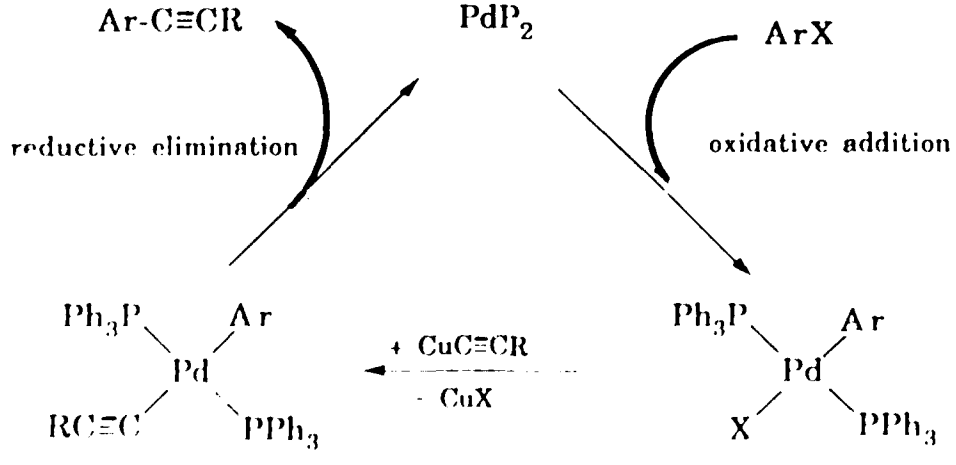


Figure 1

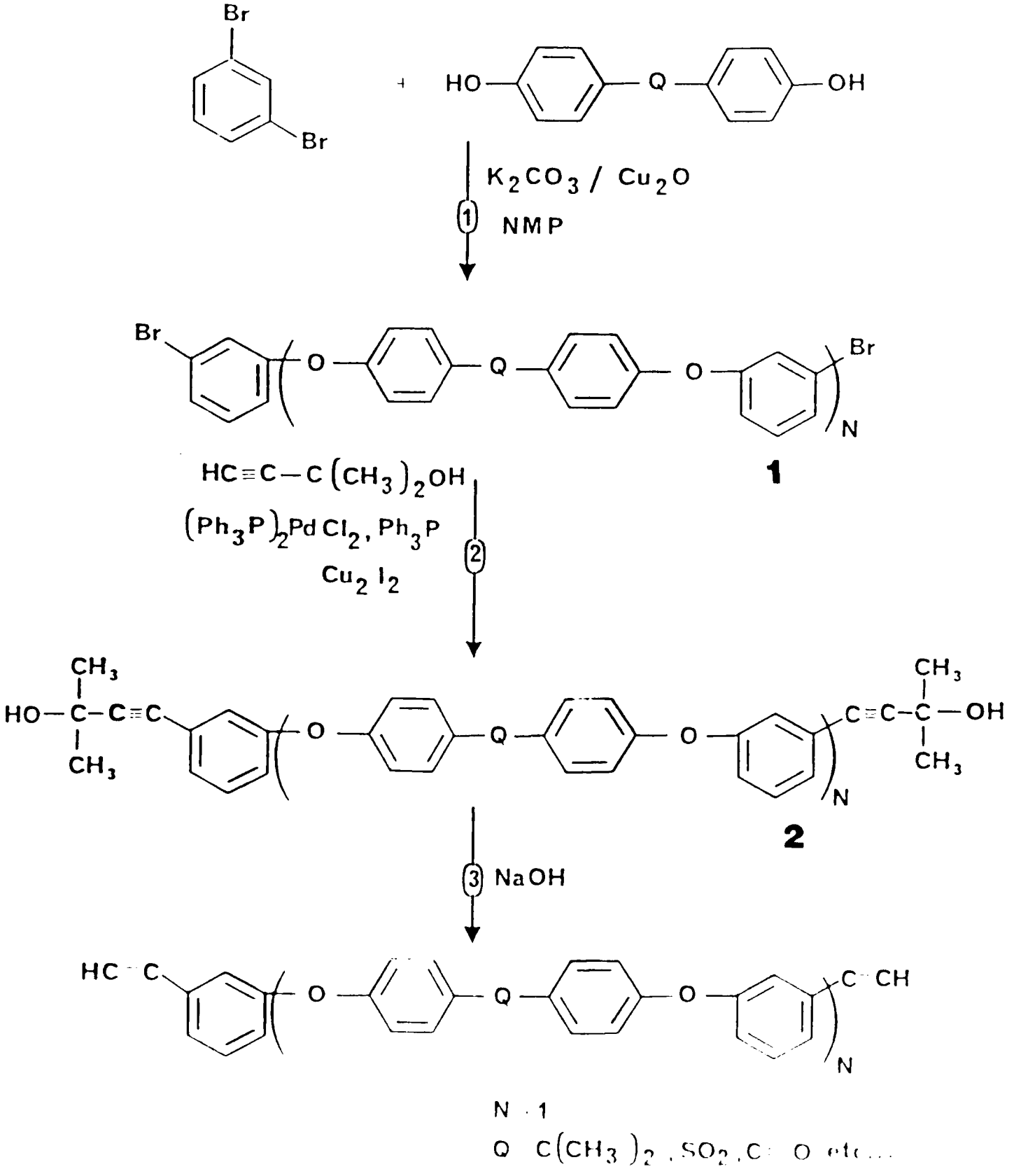

Br
Br
HO
Q
OH
K_2CO_3 / Cu_2O
1
NMP
Br
O
Q
O
Br
N
1
$HC\equiv C-C(CH_3)_2OH$
$(Ph_3P)_2PdCl_2$, Ph_3P
Cu_2I_2
2
CH_3
HO—C—C≡C
CH_3
C≡C—C—OH
2
3 NaOH
HC≡C
C≡CH
N = 1
Q = $C(CH_3)_2$, SO_2, C=O etc...

Figure 2: Evaluation of Catalyst #2
(Palladium Concentration 4.87%)

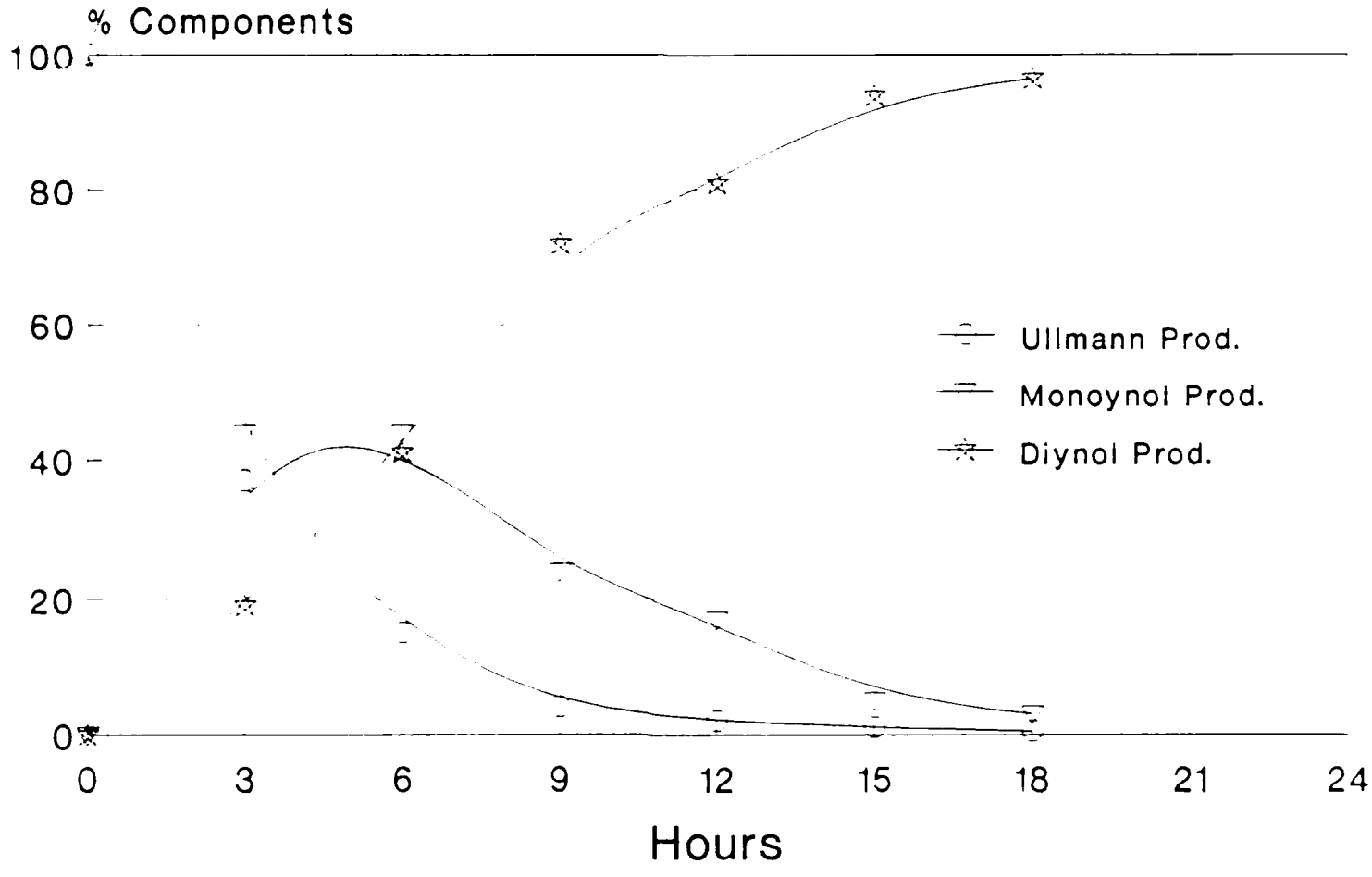
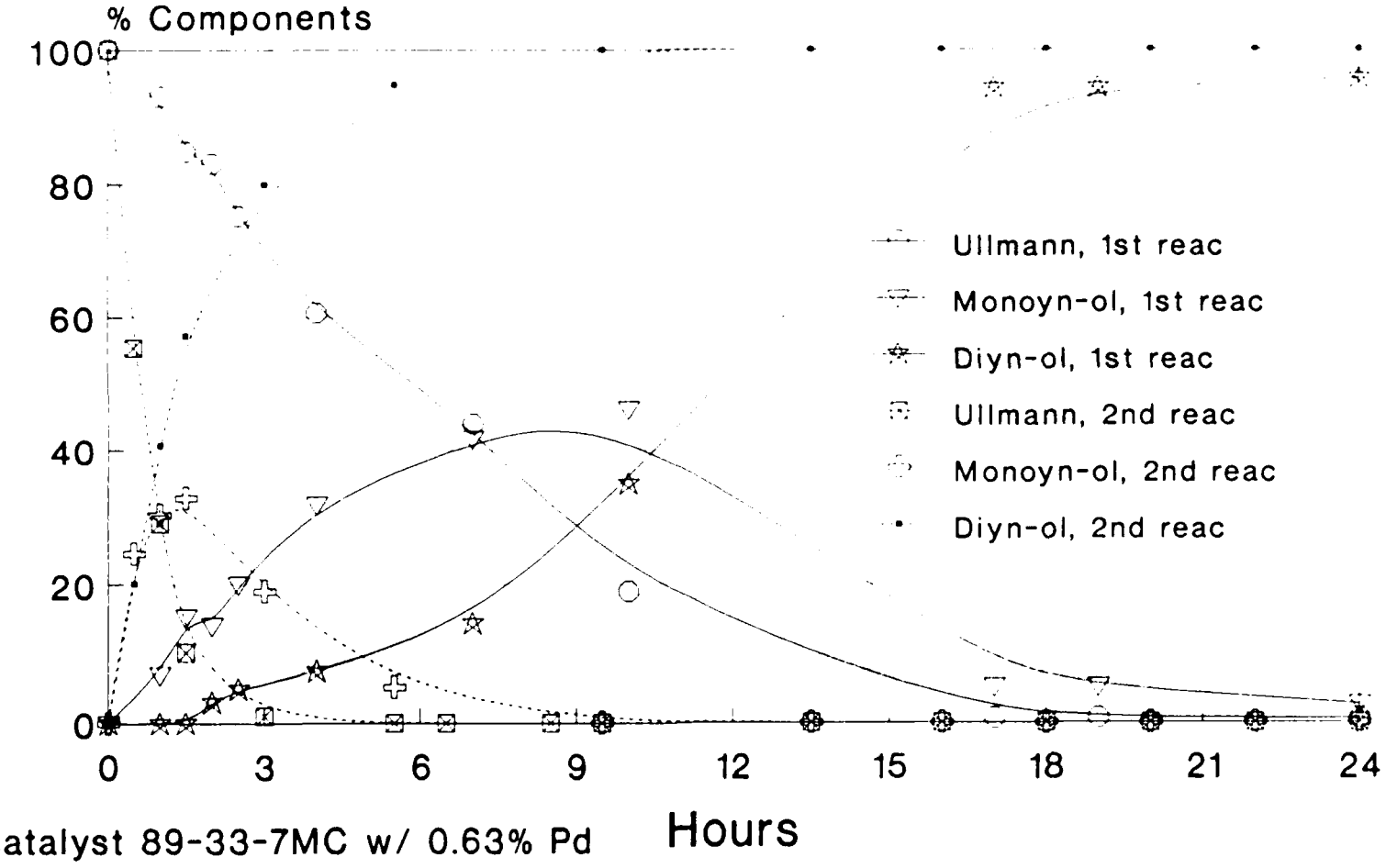


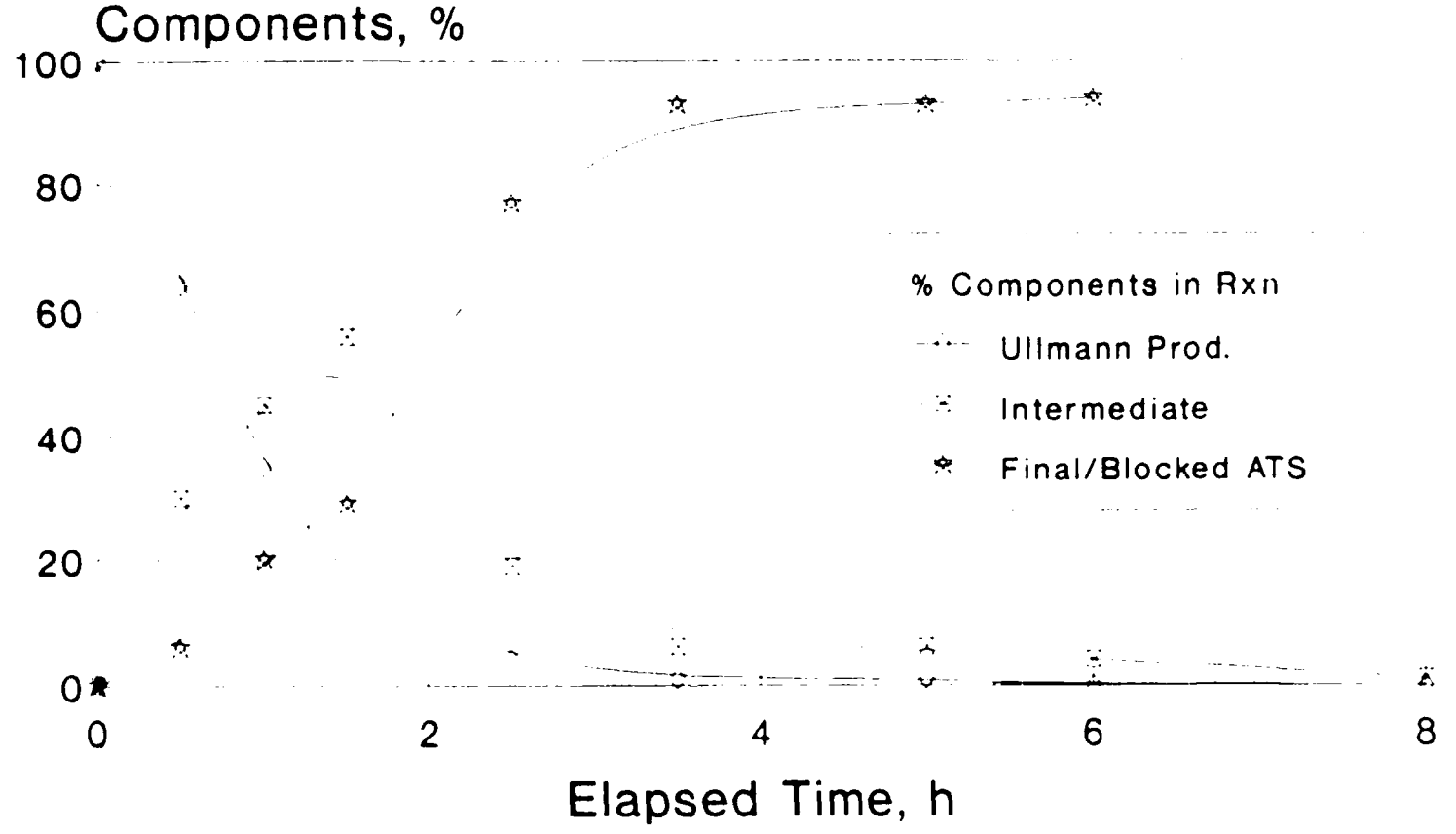
Figure 3: Evaluation of Catalyst #3
Comparison of First and Second Reaction



* catalyst 89-33-7MC w/ 0.63% Pd

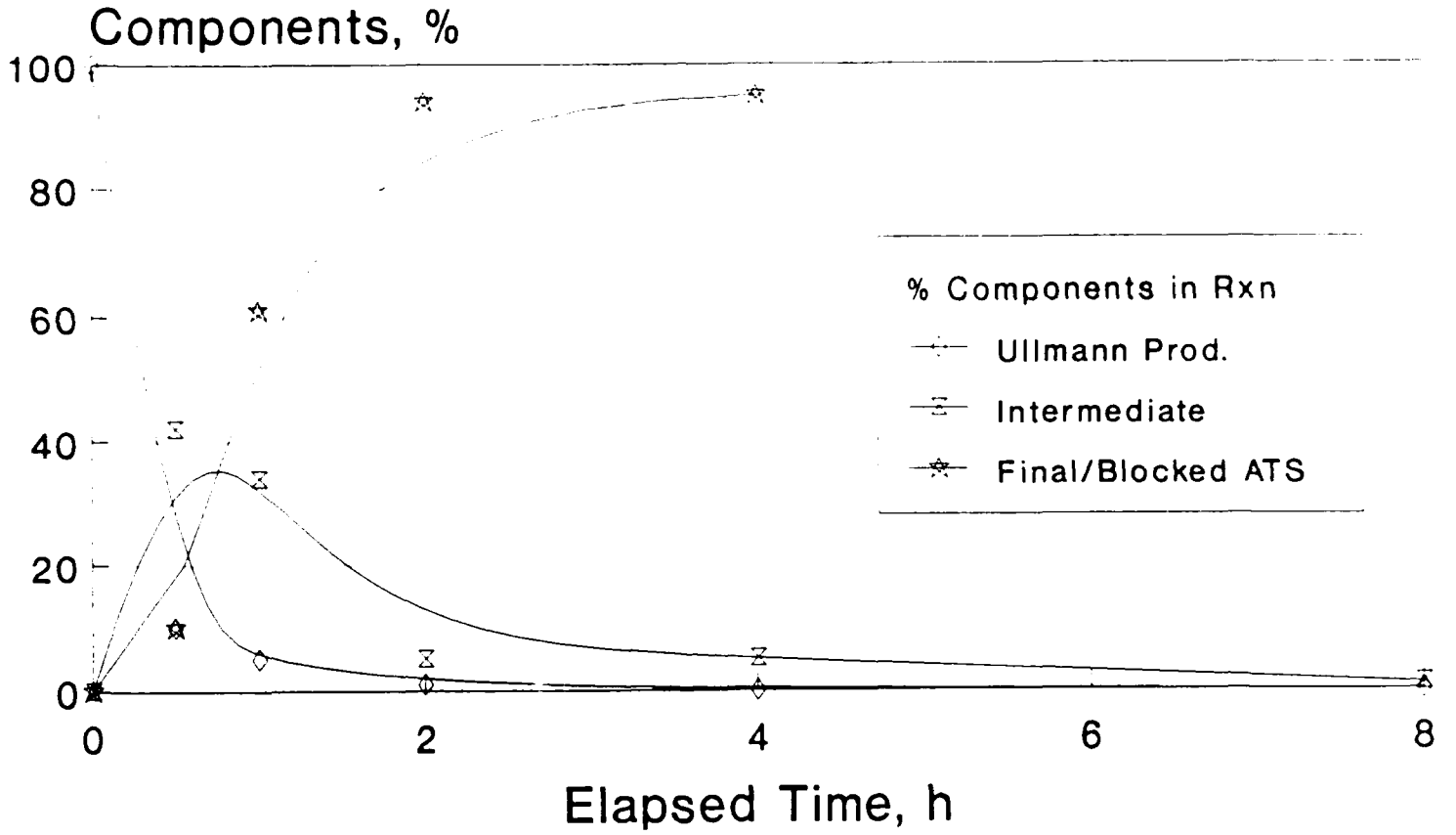
cat1ev2.cht

Figure 4A: Effect of Triphenylphosphine on the Rate of Blocked ATS Formation (Full Amount)*



* 0.0005 mole TPP/0.14 mole,Ullmann Prod

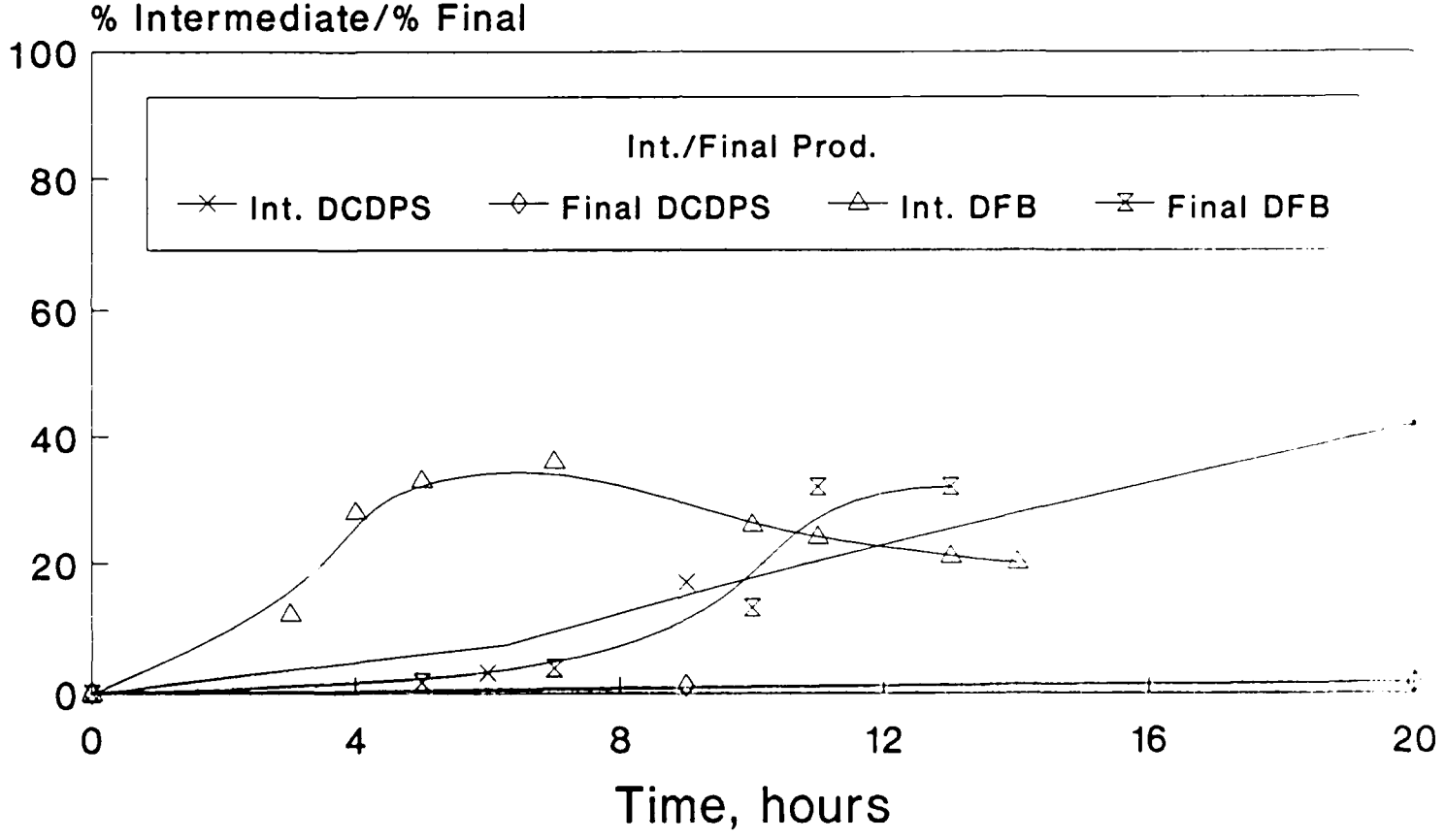
Figure 4B: Effect of Triphenylphosphine on the Rate of Blocked ATS Formation (Half TPP)*



* 0.00025 TPP/0.14 mole,Ullmann Prod

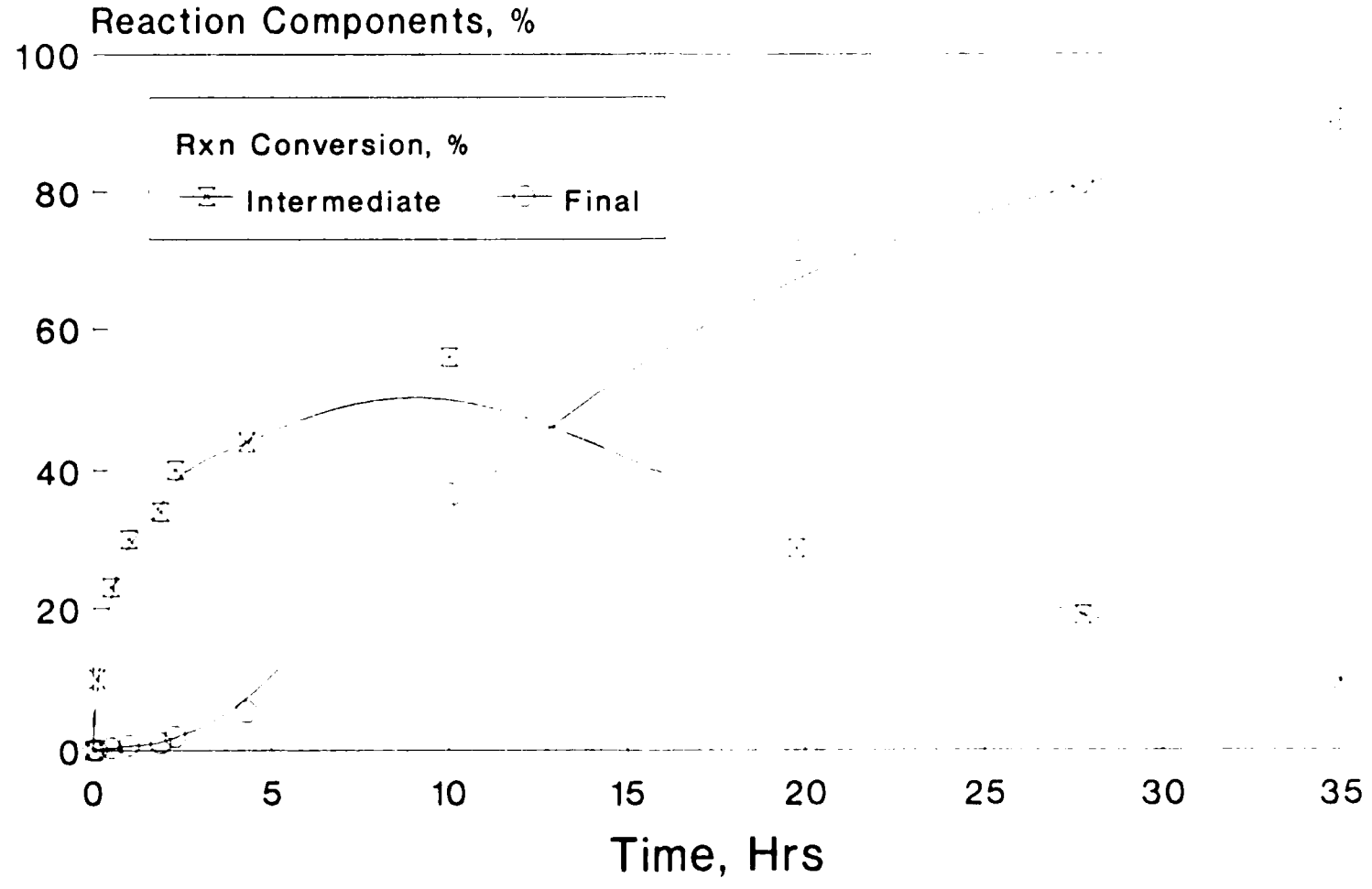
HPTPEFCT

Figure 5: Rxn of m-Cresol & Dihalides Dichlorodiphenyl Sulfone (DCDPS) Difluorobenzophenone (DFB)



CHTAP90

Figure 6: Reaction of m-Cresol & Difluorobenzophenone(Toluene:NMP;100:20)

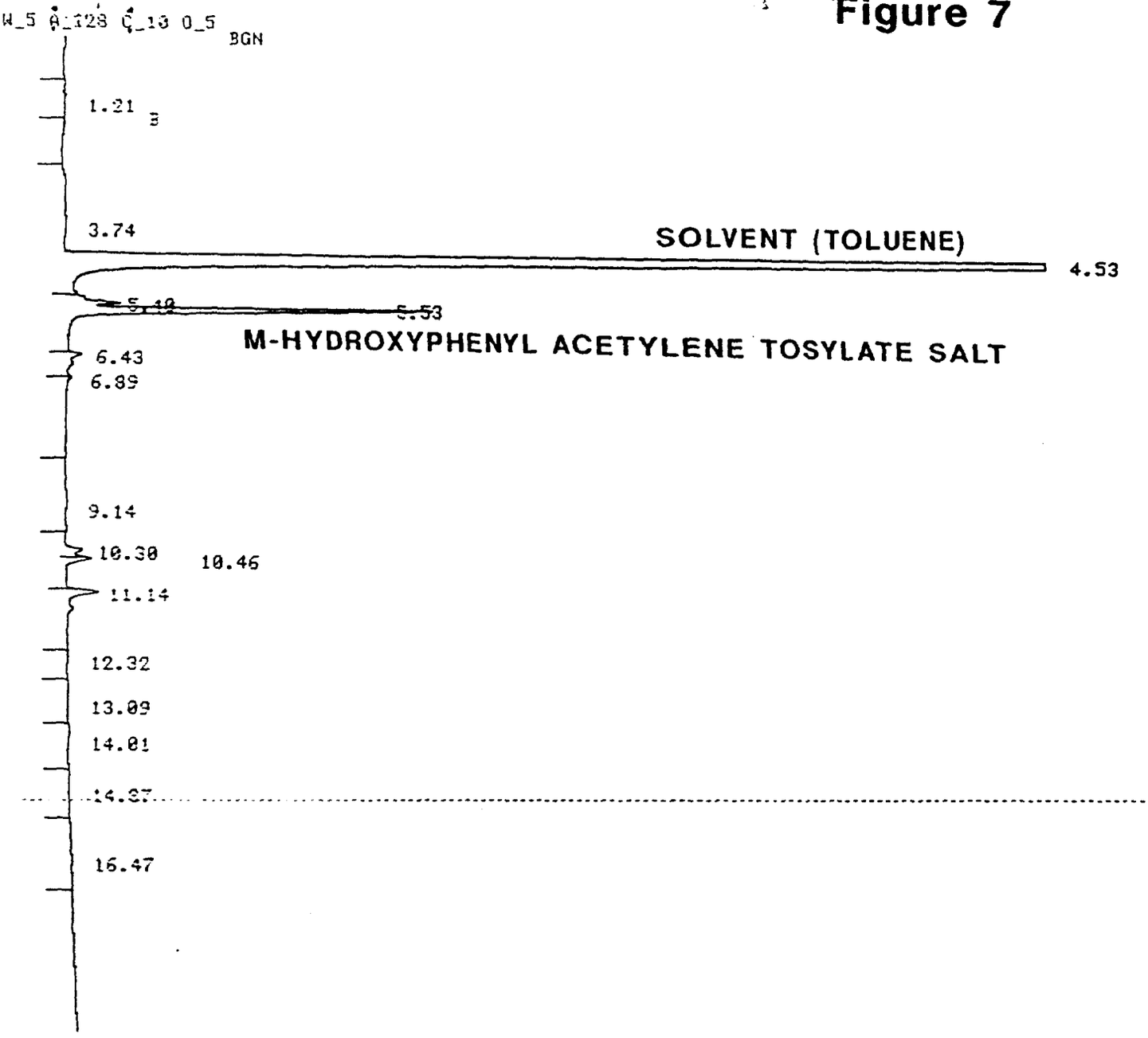


•18 CROWN 6 Catalyst

RXNCRDFB/6-90

% METHOD 1 STEWART WILLIAMS LAST EDITED 11:17.8 90/06/14

Figure 7



FILE 154 RUN 1 STARTED 15:26.3 90/06/14 RXN HYDROLYSIS12
% METHOD 1 STEWART WILLIAMS LAST EDITED 11:17.8 90/06/14

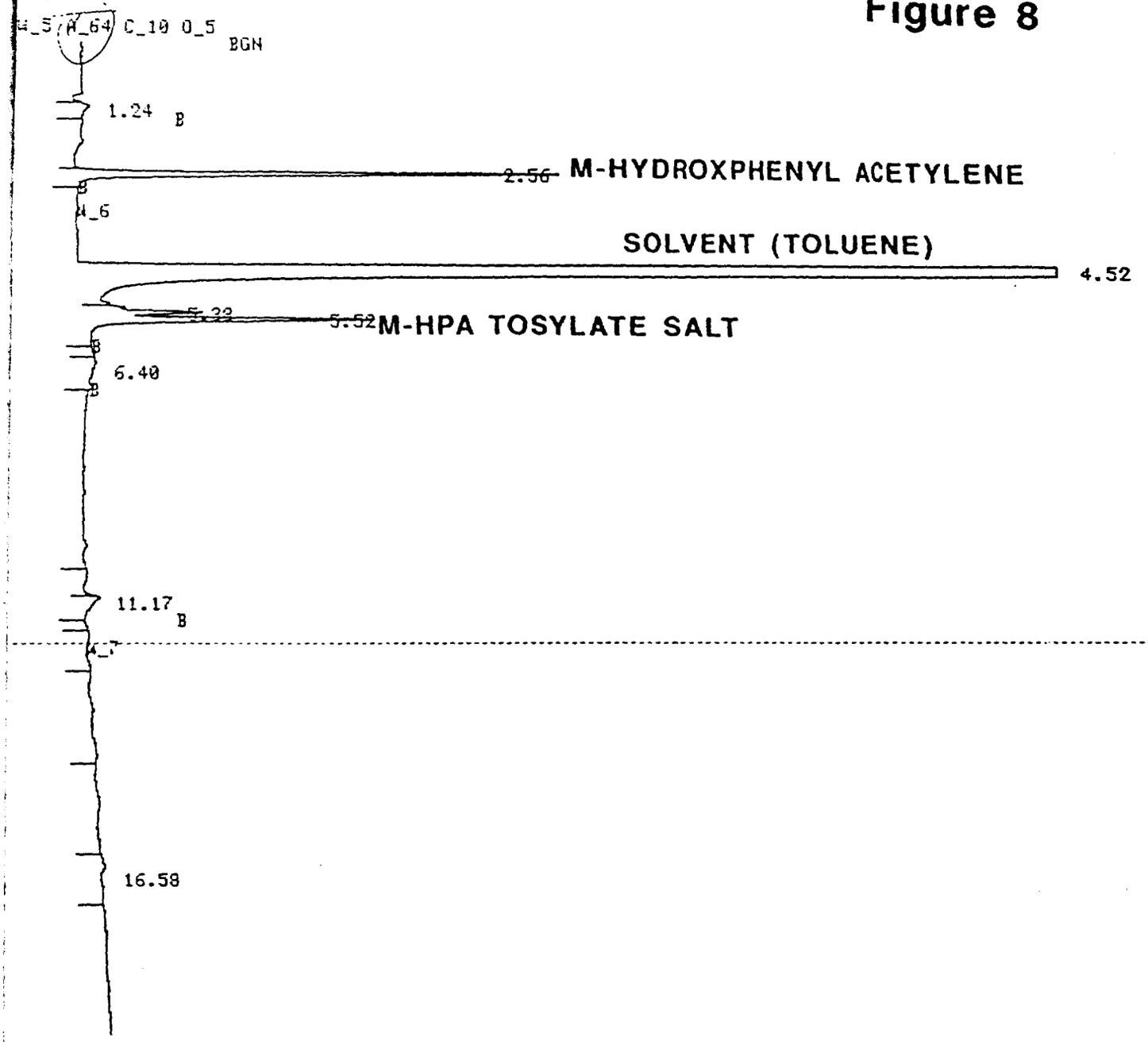
RT	AREA	HEIGHT	BC	AREA PERCENT	HEIGHT PERCENT
3.74	432316		T	1.5718	
4.53	21447408		T	77.9761	
5.40	667567		T	2.4271	
5.53	2934699		T	10.6697	
6.43	442933		T	1.6104	
6.89	376868		T	1.3702	
9.14	239849		T	0.8720	
10.30	211745		T	0.7698	
10.46	278418		T	1.0122	
11.14	473296		T	1.7208	

10 PEAKS > AREA REJECT 27505088 TOTAL AREA
0 PEAKS > HEIGHT REJECT

INTEGRATION WITH METHOD 1

FILE 17 RUN 1 STARTED 11:34.4 90/06/18 RXN 12A HYDROLYS
METHOD 1 STEWART WILLIAMS LAST EDITED 12:35.3 90/06/18

Figure 8



REINTEGRATION WITH METHOD 1

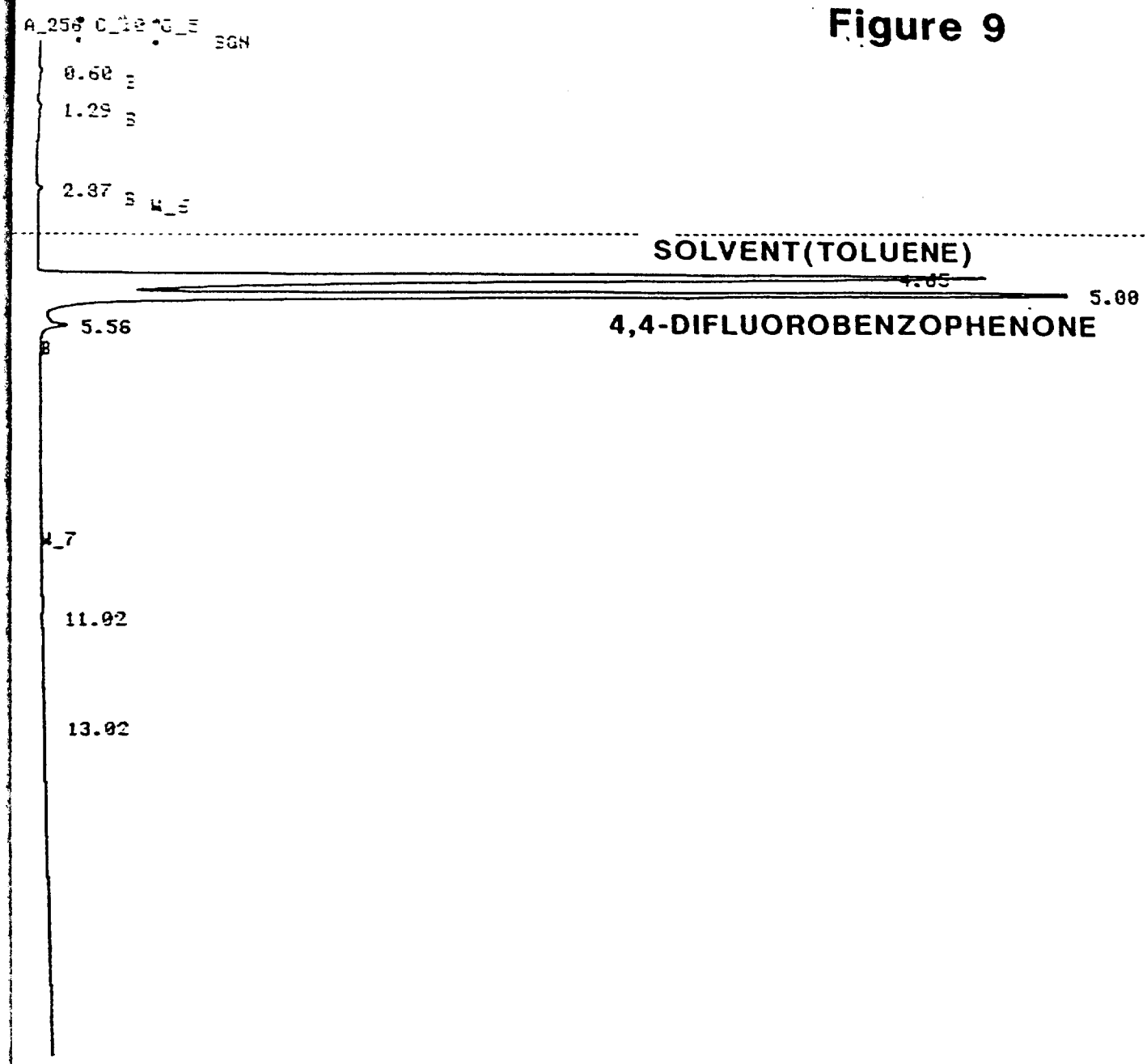
FILE 17 RUN 1 STARTED 11:34.4 90/06/18 RXN 12A HYDROLYS
% METHOD 1 STEWART WILLIAMS LAST EDITED 12:36.3 90/06/18

RT	AREA	HEIGHT	BC	AREA PERCENT	HEIGHT PERCENT
2.56	1463092			5.5681	
4.52	23029012		T	87.6418	
5.38	598247		T	2.2768	
5.52	1054968			4.0145	
11.17	130963			0.4984	

5 PEAKS > AREA REJECT 26276278 TOTAL AREA
0 PEAKS > HEIGHT REJECT 0.0000 TOTAL HEIGHT

METHOD 1 STEW J WILLY LAST EDITED 16:26.0 90/07/19

Figure 9



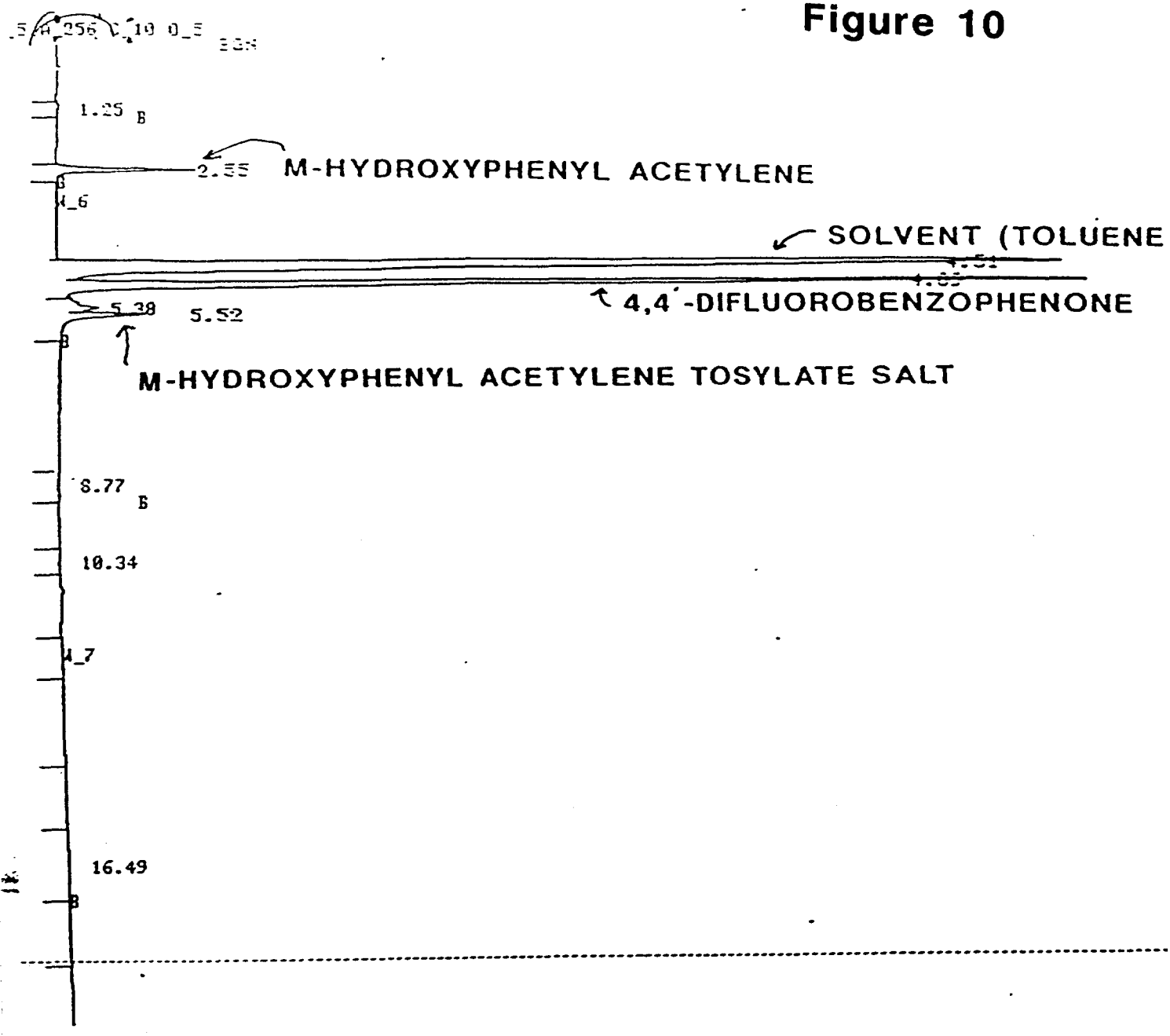
TEGRATION WITH METHOD 1

ILE 45 RUN 3 STARTED 16:05.1 90/07/19 STEW RESEARCH
METHOD 1 STEW J WILLY LAST EDITED 16:26.0 90/07/19

RT	AREA	HEIGHT	BC	AREA PERCENT	HEIGHT PERCENT
.60	40178	7.4196		0.0885	0.1338
.29	68594	7.7032		0.1510	0.1390
.87	59146	11.8956		0.1302	0.2146
.85	[illegible]	[illegible]	T	[illegible]	[illegible]
.00	20594492	3194.7725	T	45.5587	57.6270
.58	645043	68.2558		1.4201	1.2312
.02	54334	3.6625	V	0.1416	0.0661
.02	45079	2.6785	V	0.0992	0.0483

8 PEAKS > AREA REJECT 45423812 TOTAL AREA
8 PEAKS > HEIGHT REJECT 5543.8818 TOTAL HEIGHT

Figure 10



INTEGRATION WITH METHOD 1

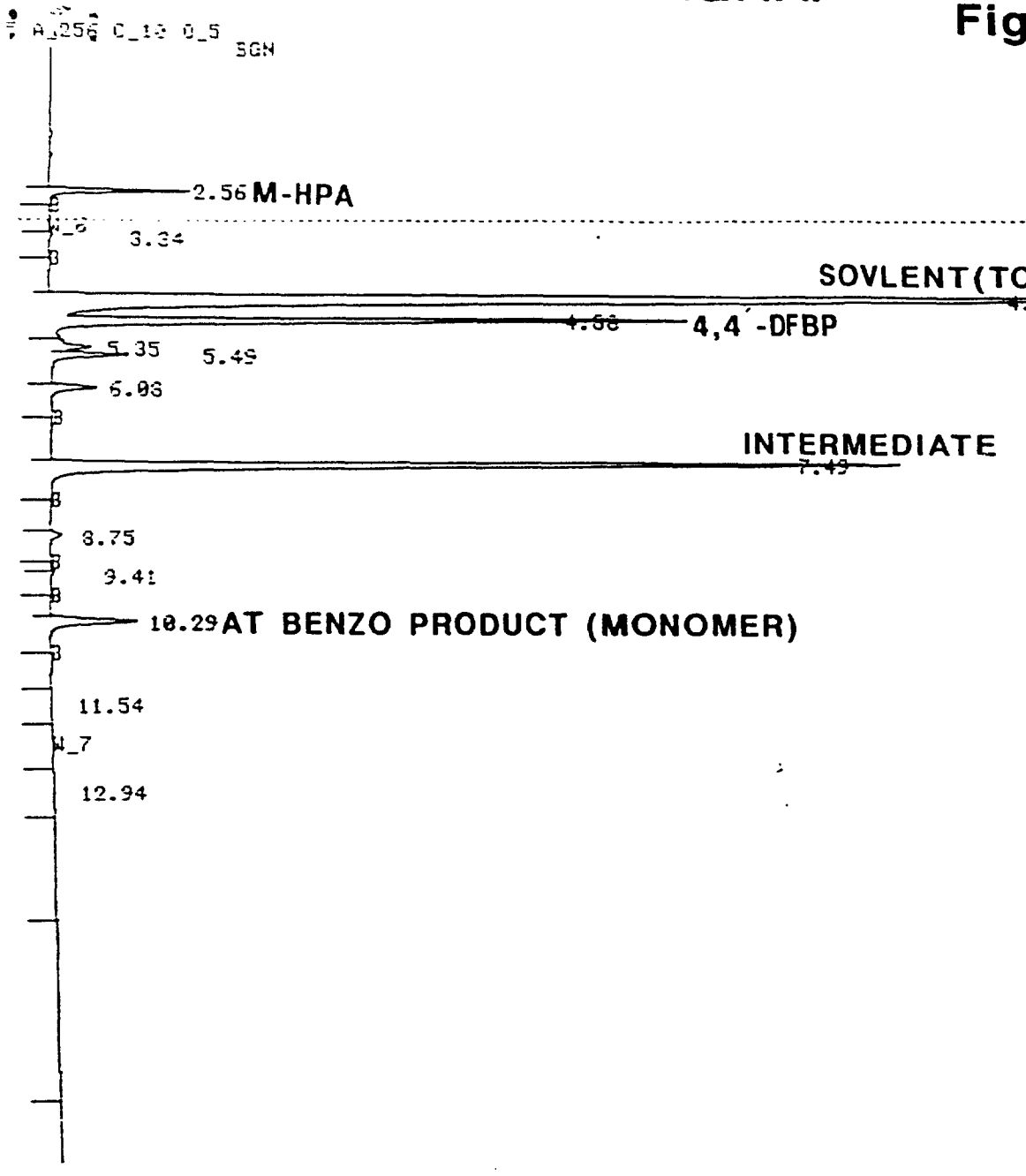
FILE 19 RUN 1 STARTED 13:25.0 90/06/18 RXN 12B CONDENS
% METHOD 1 STEWART WILLIAMS LAST EDITED 13:58.6 90/06/18

RT	AREA	HEIGHT	BC	AREA PERCENT	HEIGHT PERCENT
2.55	1661975			4.0484	
4.51	22487232		T	54.7771	
4.89	14294918		T	34.8213	
5.38	1022261		T	2.4902	
5.52	1585842			3.8630	

5 PEAKS > AREA REJECT 41052244 TOTAL AREA
0 PEAKS > HEIGHT REJECT 0.0000 TOTAL HEIGHT

FILE 34 RUN 1 STARTED 12:37.7 90/06/19 RXN12B CONDENSAT
% METHOD 1 STEWART WILLIAMS LAST EDITED 12:31.6 90/06/19

Figure 11



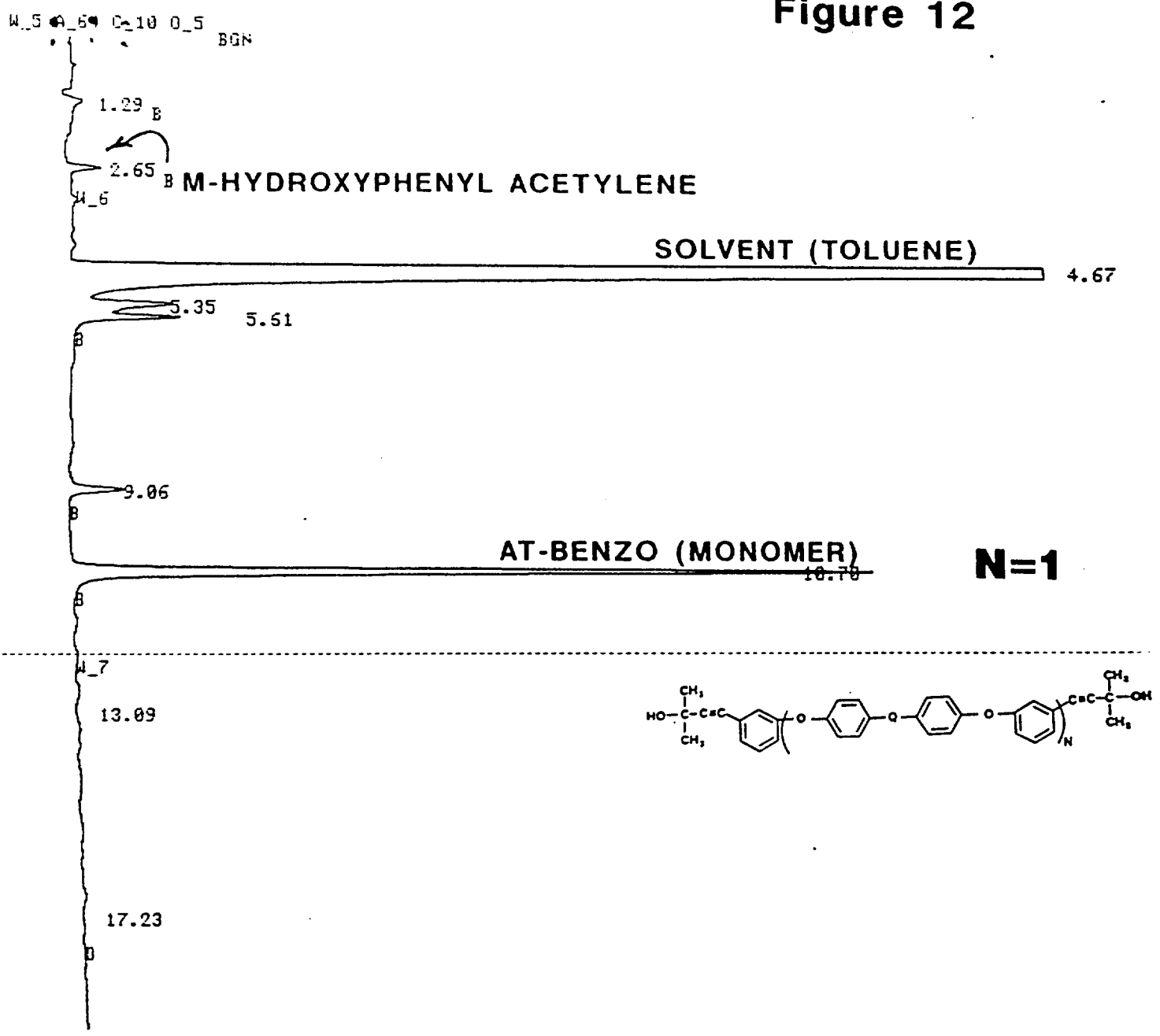
FILE 34 RUN 1 STARTED 12:37.7 90/06/19 RXN12B CONDENSAT
% METHOD 1 STEWART WILLIAMS LAST EDITED 12:31.6 90/06/19

RT	AREA	HEIGHT	BC	AREA PERCENT	HEIGHT PERCENT
2.56	1222968			2.8440	
4.51	21234574		V	49.3808	
4.88	6709325		V	15.6025	
5.35	253281		V	0.5890	
5.49	478350		V	1.1124	
6.08	602346			1.4007	
7.49	11193353			26.0305	
8.75	137050			0.3187	
9.29	1170417			2.7218	

9 PEAKS > AREA REJECT 43001652 TOTAL AREA
0 PEAKS > HEIGHT REJECT 0.0000 TOTAL HEIGHT

% METHOD 1 STEW J WILLY LAST EDITED 09:16.7 90/07/20

Figure 12



REINTEGRATION WITH METHOD 1

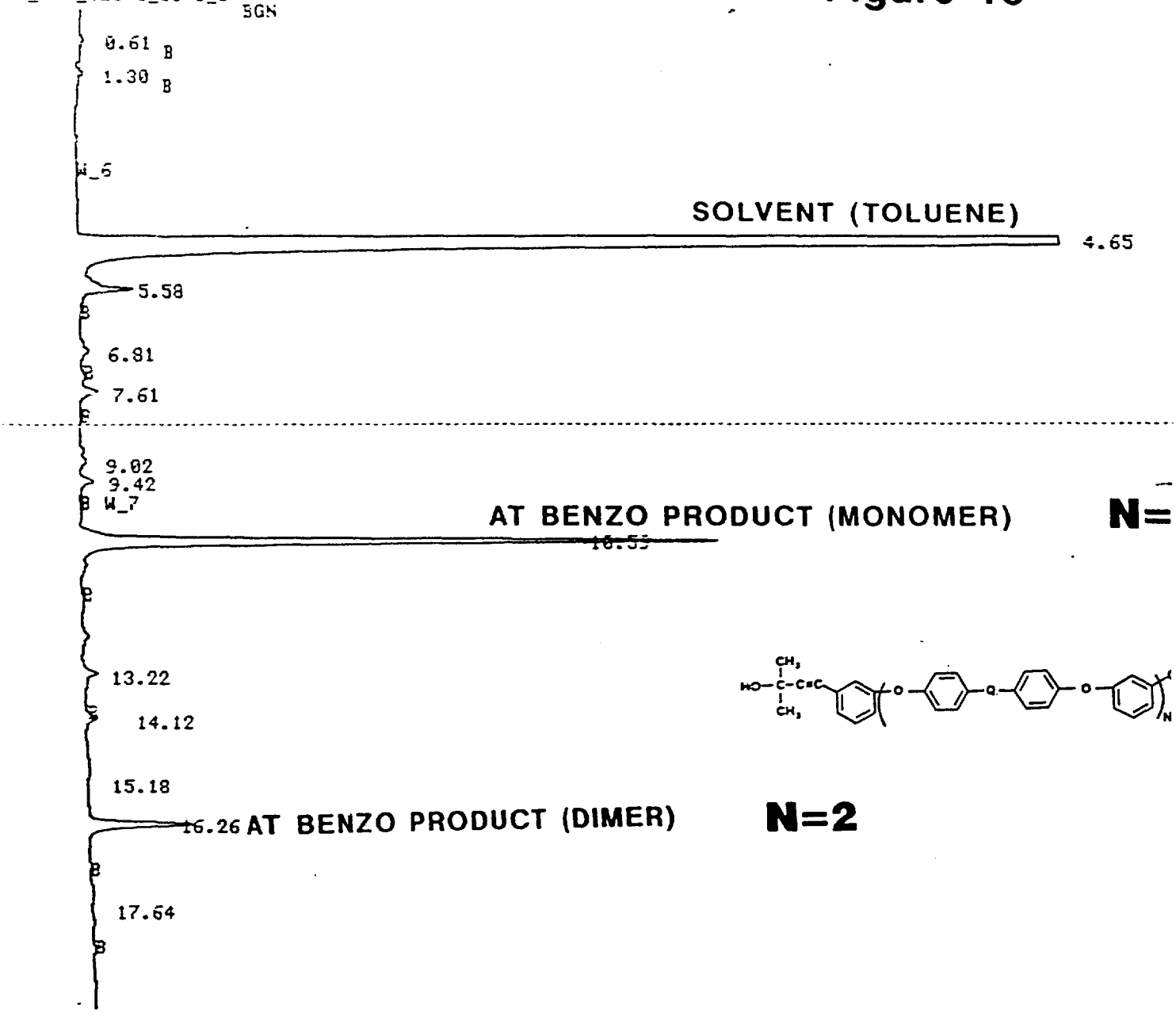
FILE 48 RUN 1 STARTED 08:45.2 90/07/20 STEW RESEARCH
% METHOD 1 STEW J WILLY LAST EDITED 09:16.7 90/07/20

RT	AREA	HEIGHT	BC	AREA PERCENT	HEIGHT PERCENT
1.29	96056	10.0284		0.3255	0.3460
2.65	129604	20.6937		0.4392	0.7140
4.67	24002448	2192.4126	T	81.3480	75.6477
5.35	709268	64.8093	T	2.4004	2.2362
5.61	530460	69.6542		1.7978	2.4034
9.06	250445	35.0586		0.8488	1.2097
10.70	3699887	500.8433		12.5395	17.2812
13.09	53347	2.5413	V	0.1808	0.0877
17.23	35391	2.1482		0.1199	0.0741

9 PEAKS > AREA REJECT 29505902 TOTAL AREA
9 PEAKS > HEIGHT REJECT 2898.1899 TOTAL

FILE 42 RUN 1 STARTED 14:29.0 90/07/19 STEW RESEARCH
% METHOD 1 STEW J WILLY LAST EDITED 14:28.2 90/07/19

Figure 13



FILE 42 RUN 1 STARTED 14:29.0 90/07/19 STEW RESEARCH
% METHOD 1 STEW J WILLY LAST EDITED 14:28.2 90/07/19

RT	AREA	HEIGHT	BC	AREA PERCENT	HEIGHT PERCENT
0.61	39151	5.9794		0.1142	0.1791
1.30	51518	6.5819		0.1502	0.1972
4.65	25861420	2261.4592	T	75.4119	67.7546
5.58	685715	65.1573		1.9995	1.9521
6.81	74379	9.8806		0.2169	0.2960
7.61	138935	18.9742		0.4051	0.5685
9.02	49064	6.2013	V	0.1431	0.1858
9.42	120479	15.0793		0.3513	0.4518
10.59	5894307	783.9380		17.1878	23.4872
13.22	122401	16.4158		0.3569	0.4918
14.12	96932	12.0364	V	0.2827	0.3606
15.18	105071	3.4517	V	0.3064	0.1034
16.26	1054185	130.2057		3.0740	3.9010
17.64		2.3622			0.0708

13 PEAKS > AREA REJECT 34293548 TOTAL AREA
14 PEAKS > HEIGHT REJECT 3337.7222 TOTAL HEIGHT

TABLE 4

EVALUALTION OF PE-SUPPORTED PALLADIUM CATALYSTS FOR AT RESIN SYNTHESIS

CATALYST	CYCLE #	PD CONC IN THE CATALYST		REACTION TIME (H)		PD CONTAMINATION IN PRODUCT, ppm
		BEFORE THE REACTION	AFTER THE REACTION	50% CONVERSION	100% CONVERSION	
Catalyst Sample # 3	1	1.61%	0.69%	12.00	>24	290
	2	0.69%	0.42%	1.50	9.5	<43
	*3					
Catalyst Sample # 4	1	0.67%	0.19%	2.50	12	29
	*2	0.19%				
	3					
Catalyst Sample # 2	1	4.87%	0.51%	7.50	>18	76
	*2	0.51%				
	3					

* Palladium concentration was too low to recycle the catalyst further.

7/15/90
FILE: PCCA.WK1