THERMODYNAMICS OF POLYMERS AND POLYMER SOLUTIONS

BY

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ABSTRACT

Using a new design of beaker tests, it was possible to run well-controlled experiments to determine potential solvents for polybenzothiazole (PBT). At the end of experimentation it was concluded that *α*-chlorotoluene (benzyl chloride) and *o*-chlorophenol are not commercially viable solvents for PBT, contradicting earlier speculations.

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INTRODUCTION

Polymers come in many different shapes and sizes and are used in a variety of ways: rubber for use in automobile tires; polyvinylchloride (PVC) in water pipelines; rayon and nylon in today's fabrics; different oils and shellacs for coating surfaces; and adhesives in the form of epoxies or some type of resin. These are just a few of the polymers found on the market today.

Other important polymers are high-performance, lightweight polymers which exhibit enormous structural strength. These could be utilized in the automobile or aerospace industry to replace heavier metallic parts.

Polybenzoxazole (PBO) and polybenzothiazole (PBT) are two such polymers. They have basically the same chemical structure (See Figure 1). The difference is that where PBT has a sulfur molecule, PBO has an oxygen. Both polymers are rigid, straight, rod-shaped molecules. Their shape allows the highly-ordered packing necessary to achieve their high-strength status. This is analogous to a box of straws packed closely together. The mechanical strength obtained from this close-packing is further enhanced by the polymer's strong intermolecular forces. As a result, the polymer exhibits a large tensile strength in the axial direction of the molecules, is thermally stable in excess of 400°C, and corrosion resistant.

Methods of manipulation or fabrication must be developed before polymers become commercially viable. Almost all polymers can be manipulated in one of three ways: heating or melting the polymer into a pliable mass; putting it into solution, then evaporating off the solvent; or chemically forming the polymer in a molded shape. PBO and PBT decompose before they melt and chemically forming the polymer in a mold has limited applications. Therefore, these polymers must be processed using solvents. There are three known solvents for PBT and PBO: concentrated sulfuric; methylsulfonic; and chlorosulfonic acids. However, these acids are extremely corrosive and present safety problems when used in large scale operations.

Consequently, there is a desire and need to find milder solvents for PBT and PBO. This report deals strictly with the search for satisfactory solvents to be used in dissolving the PBT polymer into solution.

The present work was done in conjunction with work already begun by graduate students and post-doctoral reseach associates. The intended scope of the project included completing the solvent scans, conducting unambiguous beaker tests, and making quantitative solubility measurements.

Solvent scans are used to determine which of the possible solvents would be good solvents for PBT. A preliminary solvent scan had been completed, while inconclusive, but promising results had been obtained from the beaker tests. Therefore, the experimentation done for this research project was mainly centered around running controlled beaker tests, in hopes of obtaining conclusive results.

Quantitative solubility measurements determine the concentration of polymer in a saturated solvent. Due to the negative results of the beaker tests, these measurements were unnecessary.

THEORY OF THE SOLVENT SCAN

A solvent scan is begun by gathering gas-solid chromatographic data for a solvent (See Table A for listing of solvents run in scan). The typical flow pattern of the chromatograph can be seen in Figure 2. There are two columns in the chromatograph. One column is used as a reference column, while the other is packed with beads coated with PBT. The solvent in question is injected into the system, where a helium gas stream carries it through the polymer-packed column. An electrical output is obtained from the system and fed into a strip chart recorder, which traces the output. The retention time is measured from the chart and the retention volume can then be calculated.

$$V_g^o = Q(t_s - t_a)\, T_o/T_r \,(1/M_p)\, F_p \qquad (1)$$

V_g^o = retention volume (ml/g)
Q = flow rate of the helium (ml/sec)
t_s = retention time of the solvent (sec)
t_a = retention time of the air (sec)
T_o = reference temperature of 273.15 K
T_r = room temperature (K)
M_p = mass of the polymer in the column (g)
F_p = pressure drop correction factor

From here one can calculate the Gibb's free energy of adsorption, ΔG_{ads}, by the following equation;

$$\Delta G_{ads} = RT \ln \left[\frac{M_1 \; V_g^o}{T_o \; R/(1 \text{ atm})} \right] , \qquad (2)$$

where M_1 is the molecular weight of the solvent and T is the temperature of the column.

ΔG_{ads} is the energy required for the solvent vapor to be adsorbed by the polymer. The total value itself is made up of basically three major contributions: the induced dipole moment effect, ΔG_{ads}(dispersion); the permanent dipole moment effect, ΔG_{ads}(polar); and contributions from such specific interactions as hydrogen bonding, ΔG_{ads}(other). The sum of these contributions gives the total ΔG_{ads}:

$$\Delta G_{ads} = \Delta G_{ads}(\text{dispersion}) + \Delta G_{ads}(\text{polar}) + \Delta G_{ads}(\text{other}) \quad (3)$$

Equation (3) can be written in another form which is in terms of measurable quantities.

$$G_{ads} = a_1 \alpha_1 + b_1 \mu_1 + \Lambda_1 \quad (4)$$

In this equation a_1 and b_1 are constants, α_1 is the polarizability, μ_1 is the permanent dipole moment, and Λ_1 is the specific interaction parameter. Λ_1 includes interactions due to hydrogen bonding, charge transfer complexing, etc.. The polarizability and permanent dipole moment are measurable quantities, therefore only a method for measuring Λ_1 is needed.

The specific interaction parameter, Λ_1, can be obtained using graphical techniques (See Figure 3 A & B). A plot of ΔG_{ads} versus Λ_1 is constructed first. A reference line is drawn through the points of non-polar n-alkanes. Deviations of other points of different solvents from the reference line is called the additional Gibb's free energy of adsorption, ΔG_{add}. This value is measured and then used as the y-axis of a second graph, plotted against the permanent dipole moment. A reference line is drawn through the points representing the polar, but non-specific interacting solvents. Deviations from this reference line give the specific interaction parameter, Λ_1.

Once Λ_1 has been obtained, a mathematical relationship between the polymer and solvent is needed. It has been observed that when a solvent and polymer are miscible, their respective values for the solubility parameter, δ, are equal. This is not necessarily true for the reverse case. This equality of the solubility parameter stems from the fact that mixtures of compounds tend to seek the lowest attainable level of energy. This means if there is little difference between the G's for the polymer, solvent, and the mixture of the two, then the two will tend to be miscible. If there are large differences in the G's for the polymer, solvent, and mixture, then the polymer and solvent will tend to be immiscible.

The solubility parameter is the cohesive energy density per cubic centimeter of volume:

$$\delta = \left(\frac{E_v}{V}\right)^{\frac{1}{2}} \quad . \tag{5}$$

The cohesive energy density is the same as the energy of vaporization. Rewriting equation (5) in terms of the summation of the contributional effects, as was done in equation (3), one obtains:

$$\delta^2 = \left(\frac{E_v}{V}\right) = \delta^2_{\text{dispersion}} + \delta^2_{\text{polar}} + \delta^2_{\text{h-bonding}} \quad . \tag{6}$$

The contributions due to the dispersion forces can be omitted, since they are usually very small. Values for δ_p and δ_h for the polymer can be calculated by group contribution methods. δ_p for different solvents have been compiled by industrial research groups and are available for use by the university.

Bonner[1] has proposed the δ_h for the solvent is not a reliable parameter and that using $\Lambda_1^{\frac{1}{2}}$ would represent the interaction between the polymer and solvent more accurately. Therefore, a plot of $\Lambda_1^{\frac{1}{2}}$ versus δ_p is needed to determine the potential solvents (See Figure 4). Points representing the solvents are plotted on the graph. Then lines of constant $\Lambda_1^{\frac{1}{2}}$ and δ_p for the polymer are drawn. The closer the solvent points are to the intersection of these two lines, the better the solvent should be for that specific polymer.

(<u>NOTE</u>: <u>O</u>-chlorophenol and <u>α</u>-chlorotoluene (benzyl chloride) are relatively close to the intersection of $\Lambda_1^{\frac{1}{2}}$ and δ_p for PBT.)

BEAKER SCALE TESTS

Beaker tests are carried out in sealed vials containing polymer and solvent. These vials were placed in a hot oil bath for several hours, whereupon observations were made. A major problem was encountered in trying to obtain a reusable leak-proof seal that would withstand pressures of approximately two atmospheres inside the vial. Different seal designs using teflon tape and vial caps were tested with water as the solvent. The testing consisted of sealing the vial and placing it in an oven at a temperature of 10 to 20°C above the solvent's normal boiling point. This testing was unsuccessful. A new design using silicon rubber septums and the vial caps were successfully tested, again using water as the solvent. Using $\underline{\alpha}$-chlorotoluene (benzyl chloride) as the solvent, three vials were tested. In all three vials the solvent had dissolved the septum, creating leaks.

Due to the lack of success, the search for a reusable seal was abandoned. This resulted in the use of sealed glass tubes. Inconclusive results had been obtained from earlier testing using sealed tubes (See Table B), in which color changes were observed in the solvent and polymer. Oxidation of the solvent was suspected for causing this change. Therefore, controlled studies were to be made to either verify or invalidate the results of earlier sealed tube runs for benzyl chloride and $\underline{o}$- chlorophenol.

Blank runs with no polymer present in the tube were first made with benzyl chloride. Three tubes were sealed and placed in an oven at 185°C. After the first day a slight discoloration of the solvent was observed in all three tubes. After the fifth day of heating, all three tubes had changed to a light burnt orange color, similar to that observed in the earlier runs with PBT.

(NOTE: The time intervals used in the current testing were longer than those used in the earlier runs for each respective temperature.)

An identical blank run was made with the o-chlorophenol. On the fifth day of heating at 185°C, the contents in all three tubes had turned a dark red-brown color, similar to the previous results. In both cases, the discoloration in earlier runs was attributed to interaction between the polymer and solvent. The blank runs showed, however, that the discoloration was due, at least in part, to the decomposition of the solvent. In the case of the phenol (See Figure 5), the hydrogen was being stripped off the oxygen resulting in the formation of a phenoxide ion. Depending on the substituents in the tube, a color change will be observed. Moreover, the decomposition of the solvents was attributed to the oxygen in the system.

A new system had to be developed to eliminate the oxygen. The results of a three hour reflux in a nitrogen atmosphere showed that the decomposition of the solvent, in this case benzyl chloride, was not impeded. The discoloration of the solvent could be attributed to one of two factors: (1) back-diffusion of oxygen through the reflux condenser; (2) oxygen dissolved in the solvent. In the second, the refluxing agitated the system, enhancing the decomposition reaction. Conclusion two seemed to be the more likely of the two, therefore, the reflux system was converted into a distillation unit (See Figure 6).

The unit works as follows. Solvent is placed in the vial at the left. A nitrogen stream is blown through the system at a high flow rate to expel all air in the unit. All caps are screwed on tightly and a teflon stopcock valve is used to create a small orifice for the exiting gas. A small orifice prevents air from entering the system when using low nitrogen flow rates. The cooling water for the condensers is run through an ice bath before entering the first condenser.

Benzyl chloride was first distilled leaving an orange film and residue in the solvent vial. The distillate was clear liquid. It was decided to distill the solvent a second time to be sure all oxygen had been freed from the solvent. Upon a second distillation, the solvent vial had no trace of residue and the distillate was still a clear liquid. Three tubes were filled with the distillate. The first two were sealed in the normal manner. The third tube was purged with nitrogen gas for five minutes. The nitrogen pipet, used to introduce the gas, was removed and the distillate was placed in the tube. The pipet was immediately placed in the tube and the whole system was chilled in a bath of liquid nitrogen to freeze the solvent. Again, the pipet was removed and the tube was immediately flamed-sealed. All three tubes were placed in an oven at 180°C for five days. On the fifth day the two normally-sealed tubes had turned the light burnt orange color observed previously. The specially-treated degassed tube's contents were still a clear liquid. A similar double distillation and sealing process was carried out with o-chlorophenol as the solvent. The results were the same as for the benzyl chloride: discoloration of the solvent in the two normally-sealed tubes and clear liquid residing in the specially-treated degassed tube.

Using doubly-distilled benzyl chloride as the solvent, a sealed-tube run was to be made with ten milligrams of PBT. The PBT is in the form of fluffy flakes which makes it impossible to purge the tube with nitrogen without first putting enough solvent in the tube to weight the flakes down. A total of 5 ml of solvent was placed in the tube. The tube was completely degassed except for some bubbles trapped under the flakes. Efforts were made to jar the bubbles loose, without success. The tube was sealed anyway and placed in an oven at 180°C for five days. It was observed on the fifth day that the flakes had changed from a yellowish color to a yellow-orange color and the solvent had turned a light shade of orange. The color change of the polymer was attributed to the acidity of the solvent and that of the solvent, to decomposition brought on by the trapped bubbles. The liquid from the tube was evaporated in a beaker. The residue left by the solvent after evaporation looked the same as that of the solvent vial after one distillation.

The results obtained to that point indicated that benzyl chloride was, at best, only a very weak solvent for PBT and would not be commercially viable. Therefore, the attention of the project was turned to the o-chlorophenol system.

To eliminate the problem of purging the tube full of polymer flakes, a new system was designed that would allow continuous refluxing of the polymer and solvent directly after the second distillation was finished. The final design is pictured in Figure 7. To generate this unit from the distillation unit, the following steps were used. First, the stopcock was closed to build up pressure in the system. The nitrogen gas line was then removed from the system, being replaced by a regular cap. The gas line then replaced the stopcock and the cap on top of the column was loosened. From here, parts were easily moved around to achieve the final design.

The o-chlorophenol and PBT were refluxed for a total of eight hours. The results observed were a slight discoloration of the polymer, due to the acidity of the solvent, and no color change in the solvent.

CONCLUSION

The conclusion to be drawn from this experimentation is that neither *α*- chlorotoluene (benzyl chloride) or *o*-chlorophenol are suitable solvents for polybenzothiazole (PBT). The statement conclusively disproves earlier indications that these were solvents (See Table B). It is further concluded that if color changes of the solvent and polymer are to be used as indicators of interaction between the two, then making blank runs is imperative to assure the researcher that the color change is not due to the decomposition of the solvent.

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2. AFML-TR-77-73, USAF Material Labs, Wright-Patterson Air Force Base, Ohio, December 1977.

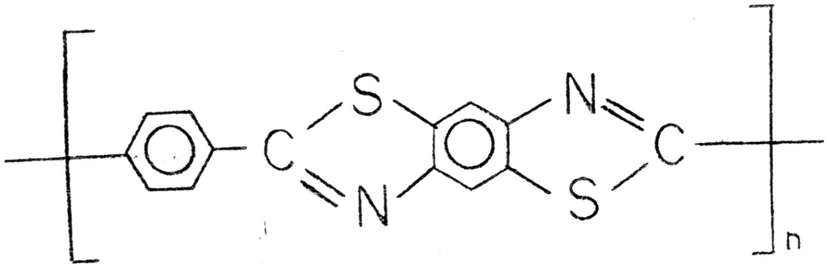
3. Principles of Polymer Systems, Rodriguez, Ferdinand, McGraw-Hill Book Co., New York, NY, 1970.

APPENDIX OF FIGURES

Figure 1 : Chemical structures of PBO and PBT

PBT

M.W. 10,000-20,000



PBO

M.W. 10,000–20,000

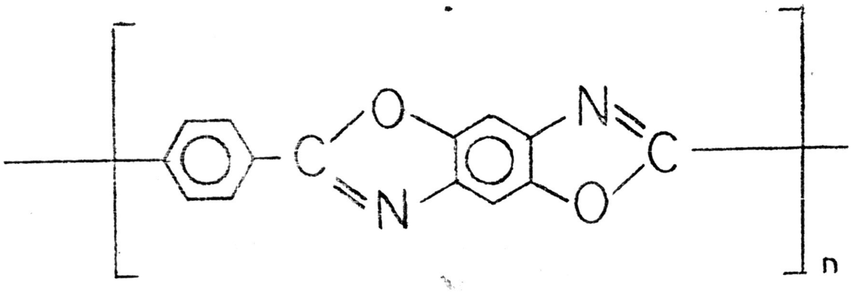


Figure 2: Gas-solid chromatography unit

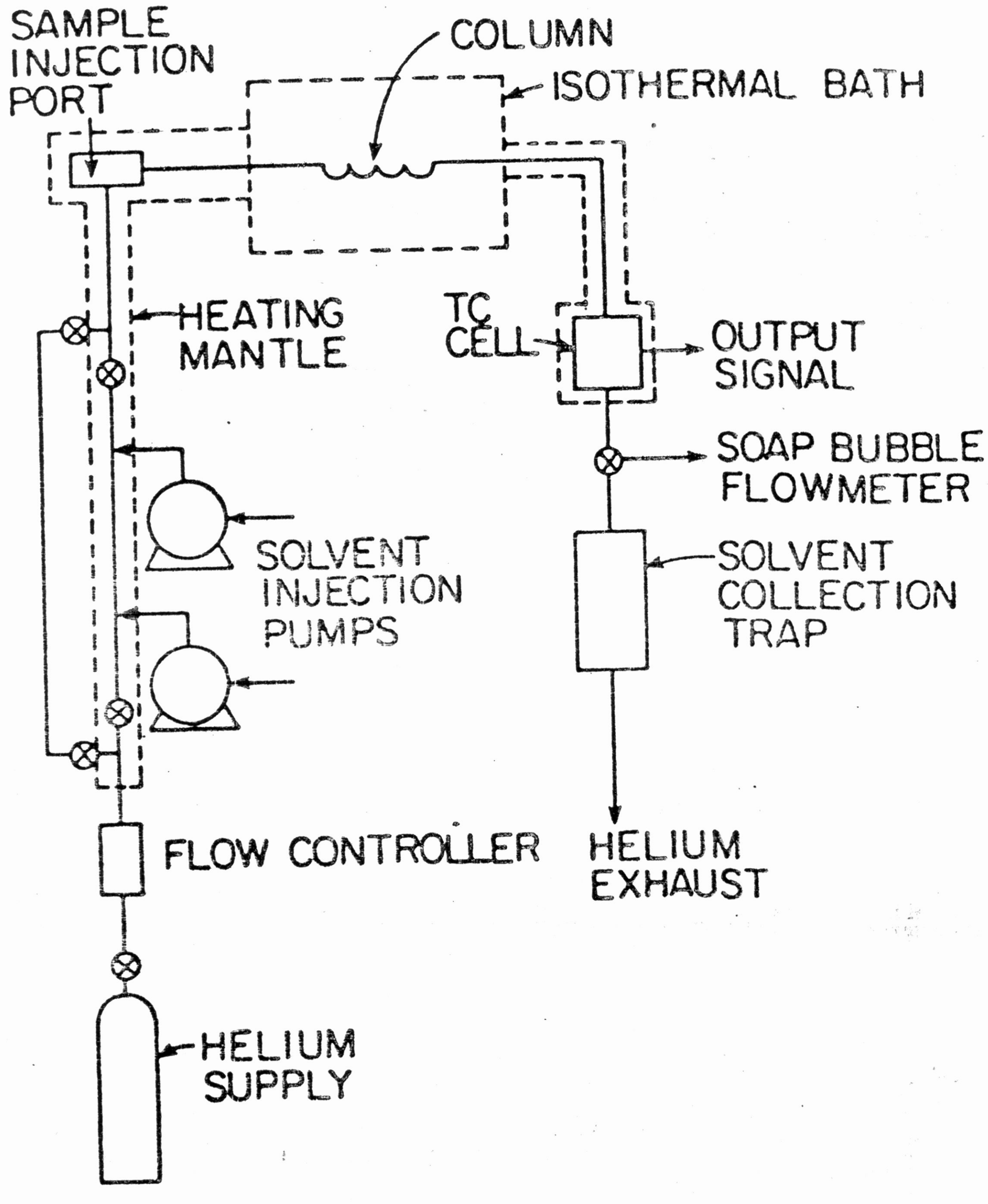
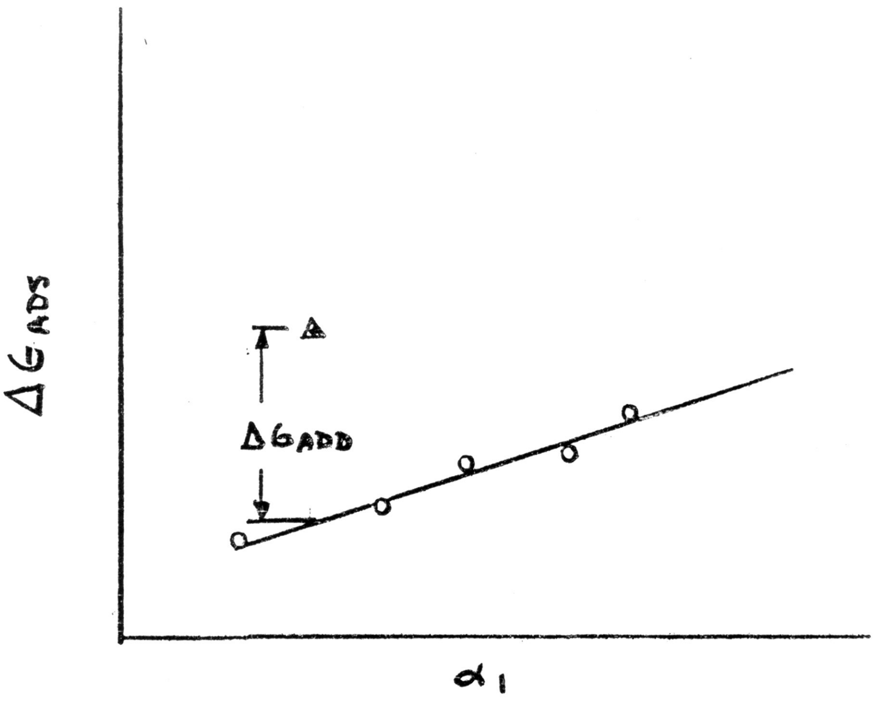
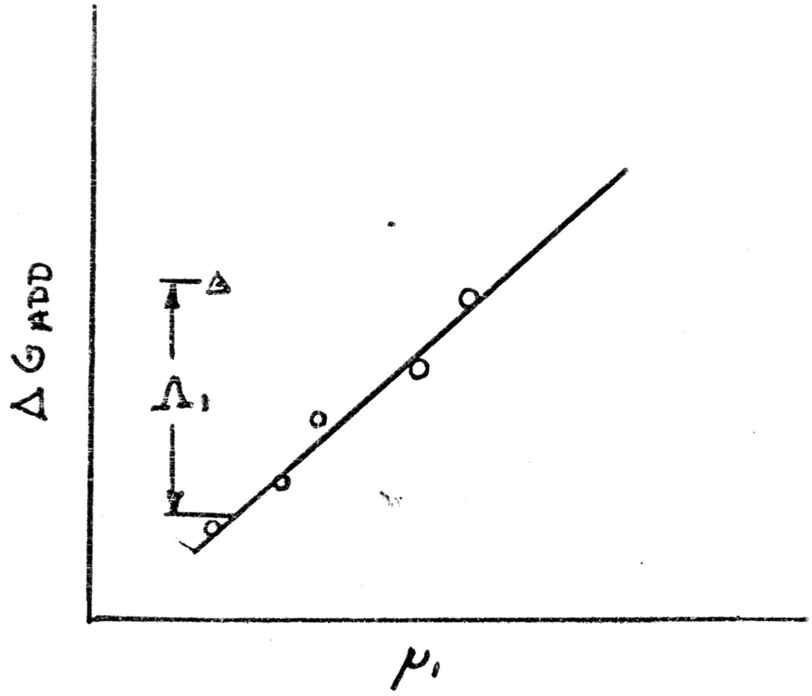


Figure 3 : A. Graphical determination of ΔG_{add}



B. Graphical determination of Λ_1



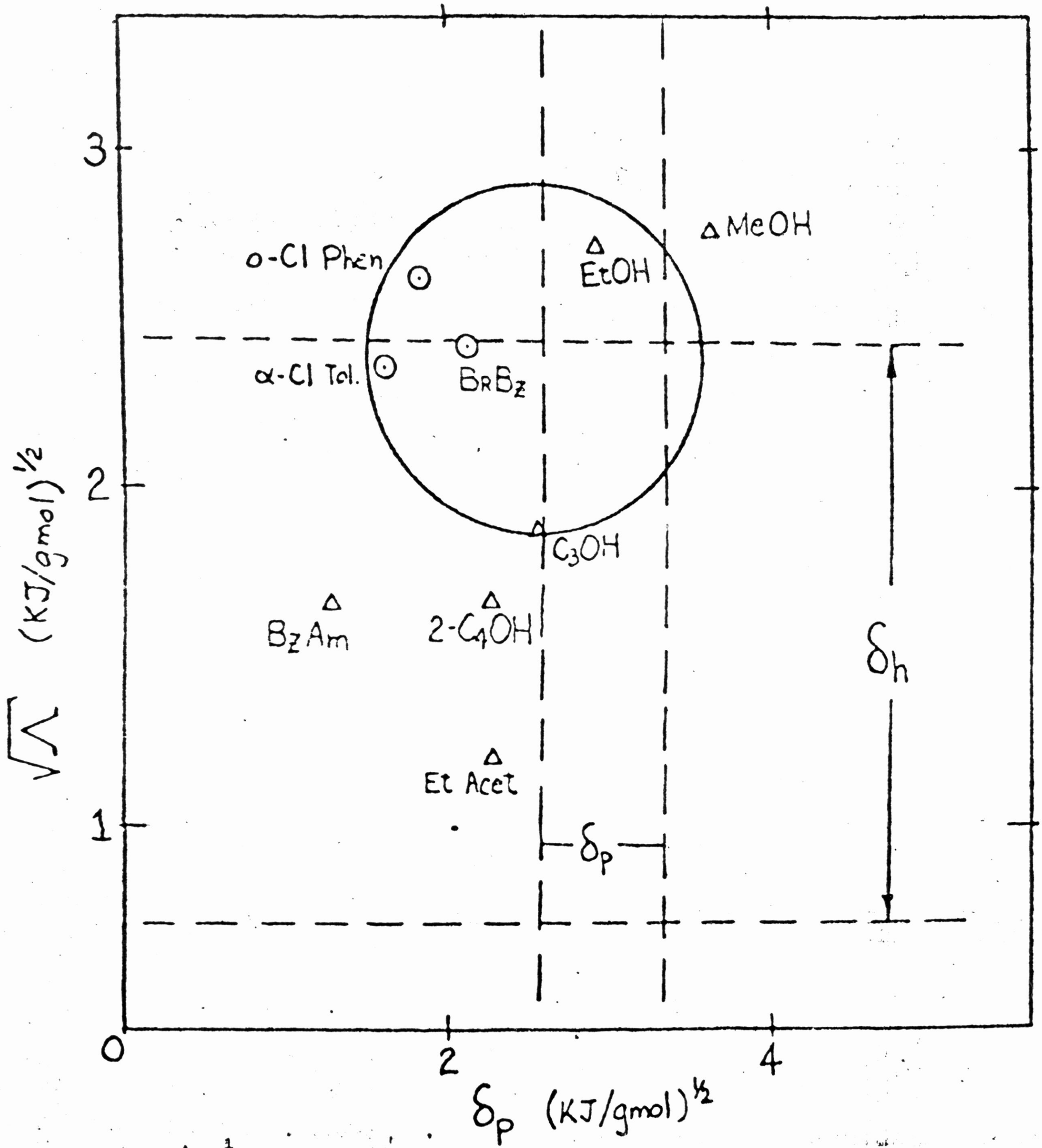


Figure 4: $\Lambda_1^{\frac{1}{2}}$ versus δ_p for PBT and various solvents

Figure 5: Formation of the phenoxide ion. Oxidation of phenols.

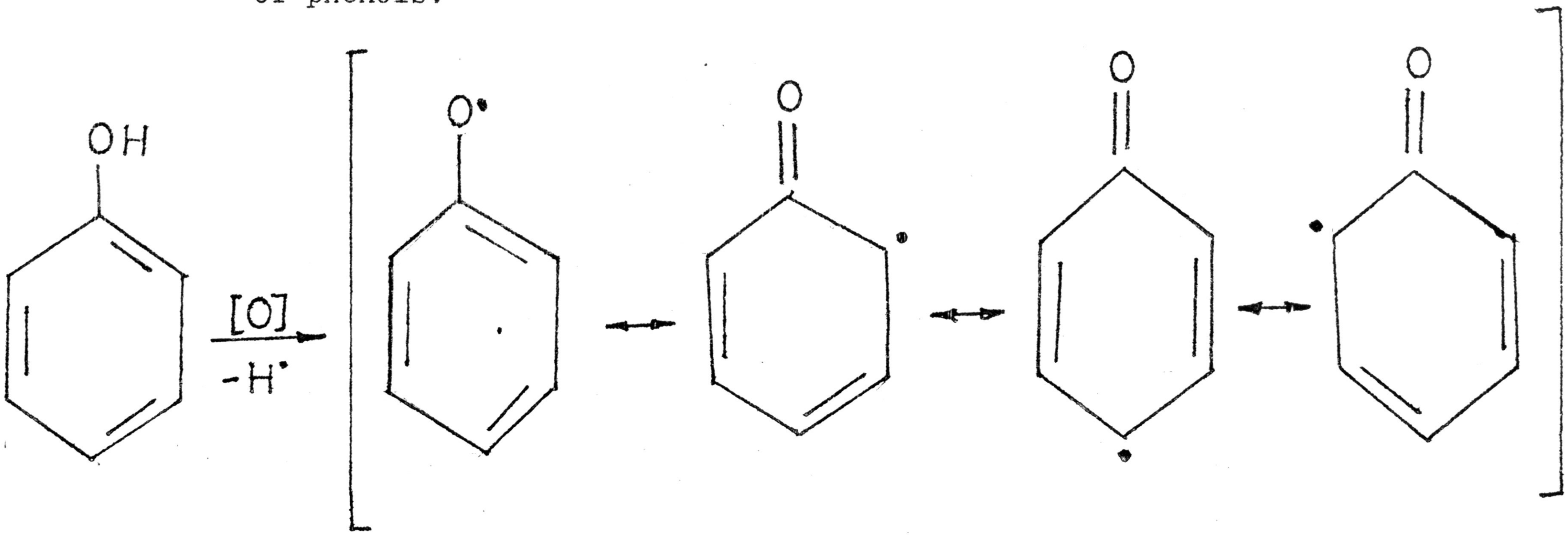


Figure 6: Distillation Unit

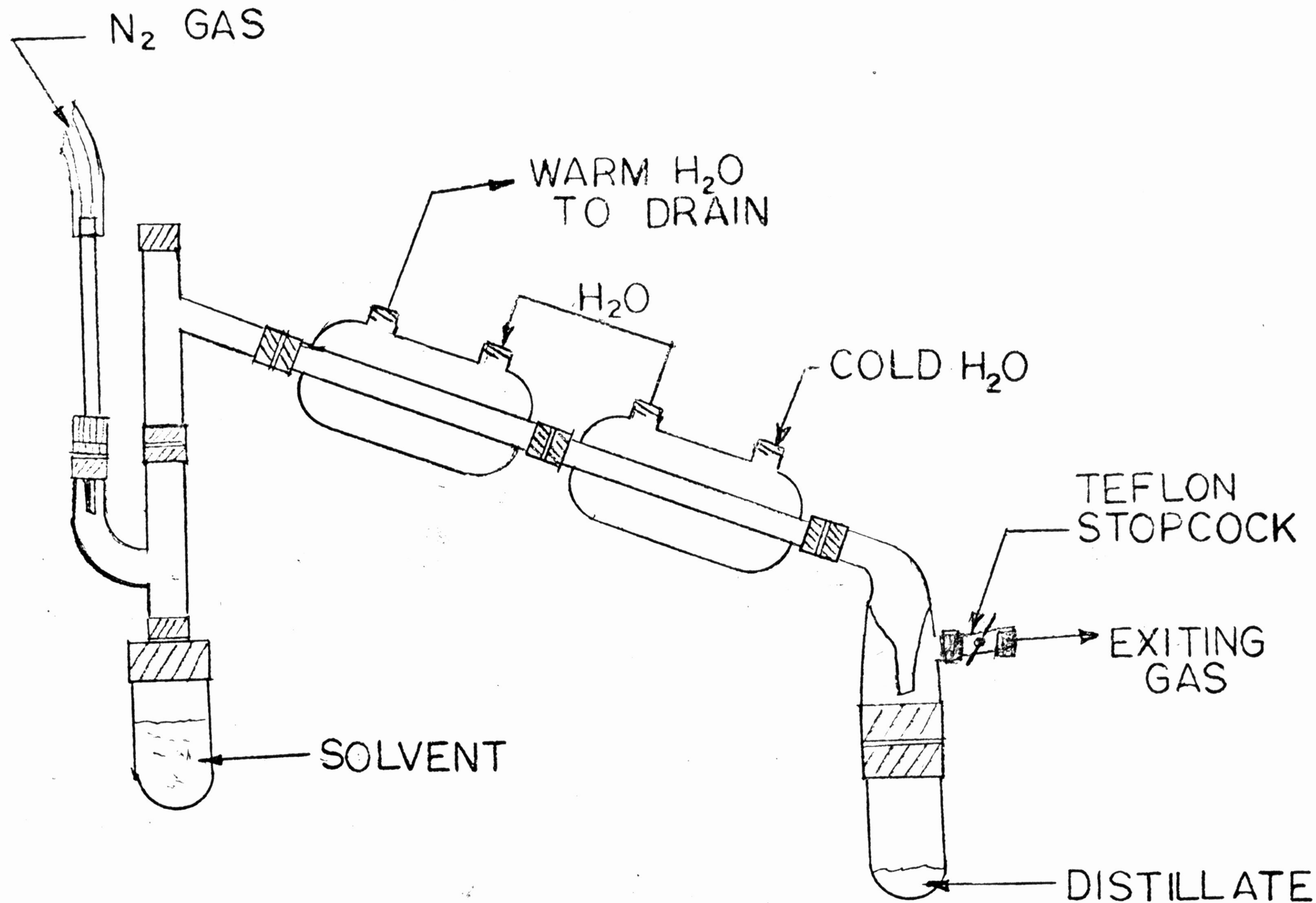
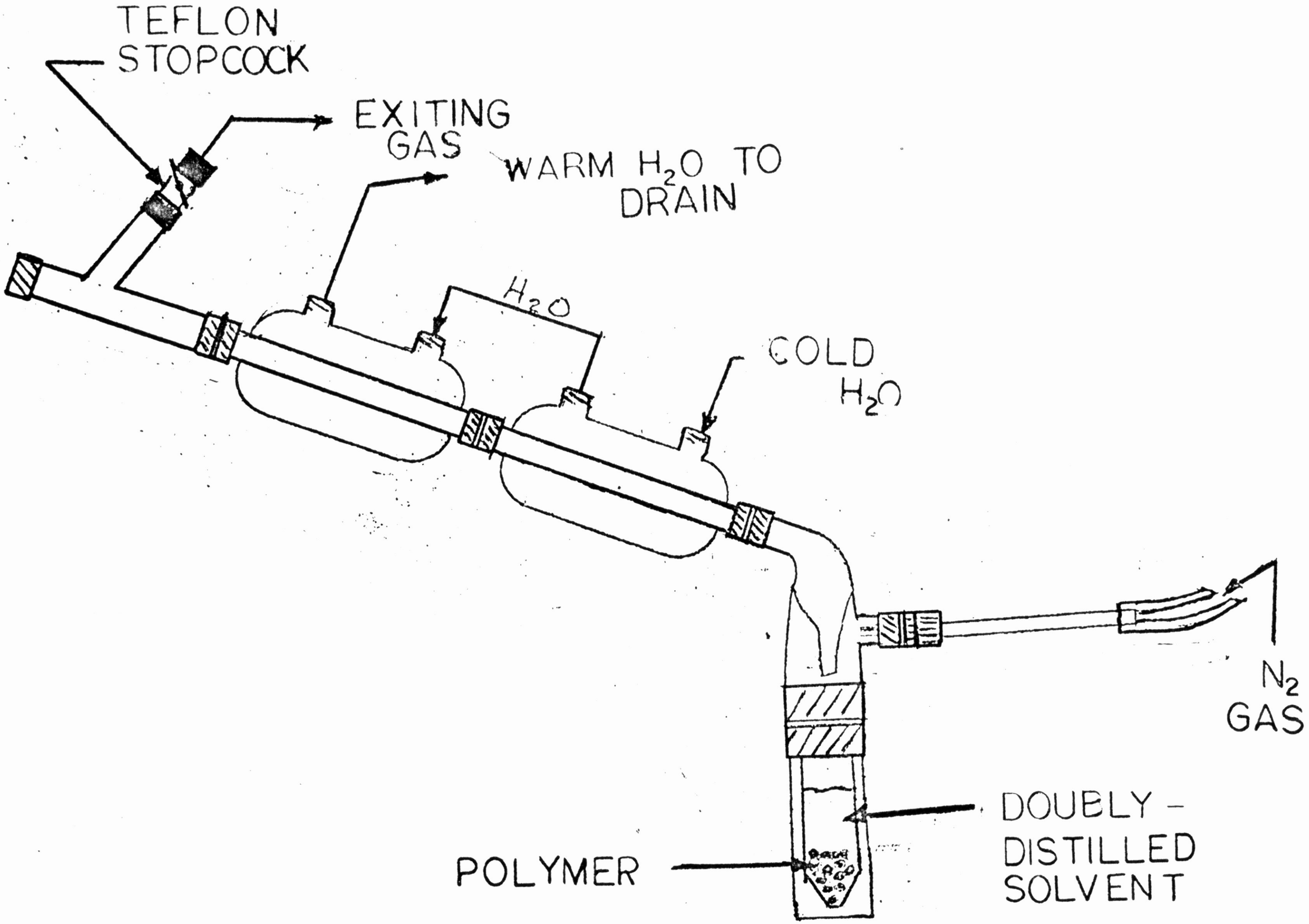


Figure 7: Refluxing Unit



APPENDIX OF TABLES

Table A: SOLVENTS SCANNED IN PBT GAS CHROMATOGRAPHY EXPERIMENT

METHANOL
ETHANOL
1-PROPANOL
1-BUTANOL
2-BUTANOL
1-DODECANETHIOL

BENZENE
BROMOBENZENE
CHLOROBENZENE
FLUOROBENZENE
TOLUENE
**A-CHLOROTOLUENE
**o-CHLORO PHENOL
m-XYLENE
FURAN
TETRAHYDROFURAN
CYCLOHEXANE
1,4-DIOXANE

DIETHYL AMINE
1,2-PROPANE DIAMINE
N-BUTYL AMINE
ACETONITRILE
PROPIONITRILE
TETRAMETHYL UREA
N,N-DIMETHYL FORMAMIDE

PROPYL ACETATE
METHYL ACETATE
ETHYL ACETATE
METHYL FORMATE
ETHYL FORMATE
N-BUTYL ACETATE

METHYL ETHYL KETONE
METHYL ISOBUTYL KETONE
DIETHYL KETONE
ACETONE

ACETALDEHYDE
PROPIONALDEHYDE

METHYLENE CHLORIDE
CARBON TETRACHLORIDE
1,2-DICHLOROETHANE
1-BROMO BUTANE
2-BROMO BUTANE
1-CHLORO BUTANE

NITRO METHANE
NITRO ETHANE
1-NITRO PROPANE

FORMIC ACID
n-BUTYRIC ACID

n-PENTANE
n-HEXANE
n-HEPTANE
n-OCTANE
n-NONANE
n-DECANE

** solvents of interest in 485 Fellows Research

Table B: SEALED TUBE TEST RESULTS

FOR SOLVENTS ON PBT

Solvent	Ambient Temp. (1 week)	120 °C (6 hrs)	190 °C (3 hrs)
Methanol	no change	no change	no change
Ethanol	no change	no change	no change
Formic Acid	color change on PBT flakes	no further change	no further change
1-Dodecanethiol	no change	no change	no change
** a-Chlorotoluene	color change on PBT flakes	some dissolution	dissolution increased
Chlorobenzene	no change	no change	
m-Dichlorobenzene	no change	slight color change on PBT	no further change
o-Dichlorobenzene	no change	slight color change on PBT	no further change
2,5-Dichloro-Benzenethiol	slight color change on PBT	intense (dark red) color on PBT	
** o-Chlorophenol	slight color change on PBT	some dissolution	considerable dissolution
Methane Sulfonic Acid	dissolves PBT immediately		
Bromo Benzene*	no change		

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* open beaker test

** solvents of interest in 485 Fellows Research