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OFFICE OF NAVAL RESEARCH

Contract Nonr 3395(00)

Task No. NR 356-431

TECHNICAL REPORT NO. 13

$B_{10}H_{12}$  Polymers: Interim Report #2

By T. L. Heying and H. A. Schroeder  
Including Work by T. A. Knowles,  
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Olin Mathieson Chemical Corporation  
Organics Division  
New Haven, Connecticut

April 15, 1963

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OFFICE OF NAVAL RESEARCH  
 Contract Nonr 3395(00)

B<sub>10</sub>H<sub>12</sub> Polymers: Interim Report #2

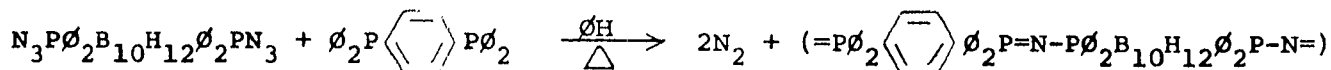
INTRODUCTION

In the preceding report on this subject (1) the major portion of the discussion centered around the polymer POP-I (-OPB<sub>10</sub>H<sub>12</sub>P-). Preliminary findings regarding PNP-II

(=P(Ph)<sub>2</sub>P=N-PB<sub>10</sub>H<sub>12</sub>P-N=) were given which were encouraging and prompted the placing of emphasis on this polymer during the intervening period.

RESULTS AND DISCUSSION

The preparation of PNP-II is conducted according to the following reaction:



In most experiments to date the product has been prepared in benzene in which it is essentially insoluble. The elemental analysis is in excellent agreement with the formula shown and its infrared spectrum reflects the presence of those linkages expected. There is no infrared evidence for the presence of

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(1) Olin Mathieson Chemical Corp., Technical Report #11 for Contract Nonr 3395(00), November 15, 1962.

residual azide linkages but the spectrum is too complex in the areas of importance to definitely state that terminal  $-P\phi_2$  groups exist (see Figure 1).

The fact that the polymer is so insoluble in benzene does not seem particularly favorable for the preparation of high molecular weight polymers. In the initial search for solvents for PNP-II there was no liquid found which appeared promising for this purpose. Subsequently, however, it was found that the polymer was soluble in chloroform ( $< 1\%$ ) and in pyridine ( $\sim 2.5\%$ ). It was experimentally verified that neither of these materials chemically interact with the polymer as has been observed when N-methylpyrrolidone and dimethylsulfoxide have been explored for this purpose. Since a suitable solvent was now available it became possible to attempt to determine the molecular weight of the polymers but the low solubility still limited the choice of methods. In such low concentrations in chloroform the light scattering method seemed applicable if the molecular weights were large enough. The first PNP-II sample so studied showed a molecular weight of 10,000 in duplicate determinations by this method. Although such values in general approach the limit of applicability of the method, it is believed that the scattering values obtained were sufficiently reliable to be meaningful. Other similarly prepared samples gave comparable values and in two instances, molecular weights of about 30,000 were obtained. Further study of samples have now indicated that PNP-II samples prepared in  $\sim 5$  gr. amounts or in 15-20 gr. amounts in benzene have molecular weights in this 10,000-30,000 range. When prepared in larger batches, the molecular weights have been apparently lower. The scattering of these samples is random and erratic and suggests that lower molecular weight material is present with the best guess being about 3000.

Other polymerization media are being sought. When the polymerization was conducted in refluxing toluene, the whole mass formed a gel rather rapidly. The polymer subsequently isolated was found to be of the "3000" molecular weight type described above. In a preparation in hot chlorobenzene, nitrogen evolution proceeded for some minutes before the polymer began to separate from solution. Although from gross appearance and infrared spectrum this material was thought to be a 'premium' polymer, it too showed a molecular weight of the "3000" type.

Further study of these various polymer samples under magnification show that on heating, the "10-30,000" polymers maintain their physical appearance and integrity to much higher temperatures than do the "3000" polymers. A more quantitative and scientific ratification of these observations is being obtained but this is a definite indication that higher stability of the polymers is favored by higher molecular weight. It is also becoming apparent that differences in the mode of preparation of PNP-II can have a decided effect on the nature of the polymers produced.

A more detailed study of the thermal behavior of these  $B_{10}H_{12}$  polymers has been undertaken. It has been known that heating POP-I and a number of related monomeric  $\begin{matrix} \phi & & \phi \\ | & & | \\ -PB_{10}H_{12}P- \\ | & & | \\ \phi & & \phi \end{matrix}$  derivatives that up to 350°C, four moles of hydrogen per  $B_{10}H_{12}$  unit are evolved. Under the same conditions PNP-II evolved only 2.4 moles in repeated experiments. When heating PNP-II (the "10-30,000" molecular weight variety) to 525°C it was repeatedly found that after about 0.5 hrs. at this temperature that 6.6 moles of gas per  $B_{10}H_{12}$  unit are evolved and no further increase in gas volume was observed. Of this gas about 8 mole percent is benzene with the remainder being hydrogen which should correspond to a weight loss of about 5 percent. On weighing the samples after heating, a loss of

11-14 percent was found leaving a discrepancy of 6-9 percent the cause of which is being sought. Thermogravimetric analysis of PNP-II also indicate an 11-14 percent weight loss at this temperature and the results of heating PNP-II mineral fiber composites (1) have given similar results.

A systematic study of the behavior of PNP-II on heating has been undertaken. Samples are brought to a specified temperature (in vacuo) and maintained for one hour. The weight loss, gas evolution and residue composition are being determined. At this writing the only complete results available are those for a "3000" PNP-II material (see Table I). These results indicate a much more extensive and continuing decomposition for

TABLE I  
Thermal Study of a "3000" PNP-II

<u>Temp. °C</u>	<u>% Wt. Loss</u>	<u>Moles Gas/g.</u> <u>x 10<sup>3</sup></u>	<u>Gas Composition,</u> <u>Mole Percent</u>
400	7.6	4.8	H <sub>2</sub> , 93; ØH, 4.3; ?*, 2.8
400	6.4	4.6	
400	5.9	4.4	
450	10.4	6.0	H <sub>2</sub> , 92.8, ØH, 6.7; ?*, 0.5
450	10.8	6.2	
500	18.3	7.5	H <sub>2</sub> , 92.4, ØH, 7.6
500	18.3	7.6	
540	25.0	8.6	incomplete
540	incomplete		

\* Appears to be acetone

this lower molecular weight material than previously observed for the samples showing higher molecular weights. When the latter type material has been treated as in Table I the extent of their difference will be known. It should be pointed out that such differences in behavior have become apparent in the preparations of composite materials discussed below. The "3000" type material invariably gives extremely poor products when compared with those made from the "10-30,000" material. Also note that acetone (used in purifying the polymer) has occurred as an off gas although adequate steps had been taken to insure its removal. This raises the question of whether all or part of the benzene found after heating these various polymer samples could have been occluded and is not really a product of decomposition. This is to be explored.

One further point regarding the TGA analysis of PNP-II is that when heated to the limit of the instrument ( $\sim 1800^{\circ}\text{F}$ ) a total of  $\sim 24$  percent of its weight had been lost but it showed no further tendency to evolve additional gases.

Since PNP-II was found to be slightly soluble in chloroform and pyridine, attempts were made to deposit coatings on metals. Such coatings were successfully prepared but proved to be too thin to be of any value. This is undoubtedly due to the low concentration of polymer and attendant low viscosity of the solution. Attempts to build up the thickness of the coatings by successive application were not successful.

The prime interest in applications of PNP-II remains in the preparation of composite materials with mineral fibers. Two inch diameter discs are now prepared for study and a more suitable mold for the preparation of evaluation studies has been received. As discussed below, the 'curing' is completed at  $425^{\circ}\text{C}$  which is quite rough on a mold and the steel for construction of such items should be chosen with care.

An evaluation disc is usually prepared in the following manner. The polymer and the fiber are intimately mixed in the desired proportions and a small quantity of a liquid (N-methylpyrrolidine and toluene have been used) is added to allow the solids to be compacted into the mold. The mold is prepared by coating the parts with a silicone mold release agent and the faces of the pistons are covered with thin aluminum foil to further insure that the sample does not adhere to the mold. After loading, the mass is compressed to 5000 psig. The mold is clamped and placed in an oven at 150°C for 0.5 hrs. during which time the "slurrying agent" and any other extraneous volatiles are expelled. Additional pressure is applied to the mold which is then gradually heated from 175°C to 425°C during about two hours and kept at the latter temperature for an additional 0.5 hours. After cooling, the specimen is easily removed from the mold.

Asbestos, refrasil and carbon fibers have been examined as filler material. Good composites with asbestos are obtained which contain 20-25 percent PNP-II. Refrasil requires 35-50 percent resin and gives nice appearing but brittle products; the silica fiber seems to be poorly wetted. Carbon fiber also requires 35-50 percent resin and gives adequate composites but since the resin is greatly absorbed by the fibers, the product is somewhat soft.

PNP-II asbestos composites containing 25 percent of the polymer have a specific gravity of  $\sim 1.6$  and show Sward hardness values of 26-32 (glass is 100). Using a Tinius-Olsen apparatus, the tensile strengths of a number of these samples were found to be in the 1200-1450 p.s.i. range. The samples for tensile testing had to be sawed from larger pieces and irregular edges have been observed. A method to minimize this has been found and pieces so cut should show still higher tensile strengths.

A series of samples were heated at 1000°F without particular precaution to completely exclude air. Their testing after heating in comparison with similar unheated samples showed that slightly less than 50 percent of their tensile strength had been maintained.

Several attempts to use PNP-II as a laminating resin for glass cloth have given some encouraging results but much additional work is required in this area. When PNP-II of the "3000" molecular weight type was used to prepare either composites or laminates, pourous and brittle products were obtained.

A consistant discrepancy in weight loss when related to gas generated has also been noted for POP-I. In this case however the magnitude of this discrepancy is only 4-7 percent. Thermogravimetric analysis of this polymer showed that at ~ 1500°F, ~ 14 percent of its weight had been lost but no further weight loss occurred up to the limit of the instrument (~ 1800°F). Although the thermal behavior of this polymer is attractive, no real utility has been discovered for it as yet.

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APPROVED BY:

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DATE: April 10, 1963

FIGURE 1

INFRARED SPECTRUM OF PNP II POLYMER (KBr Pellet)

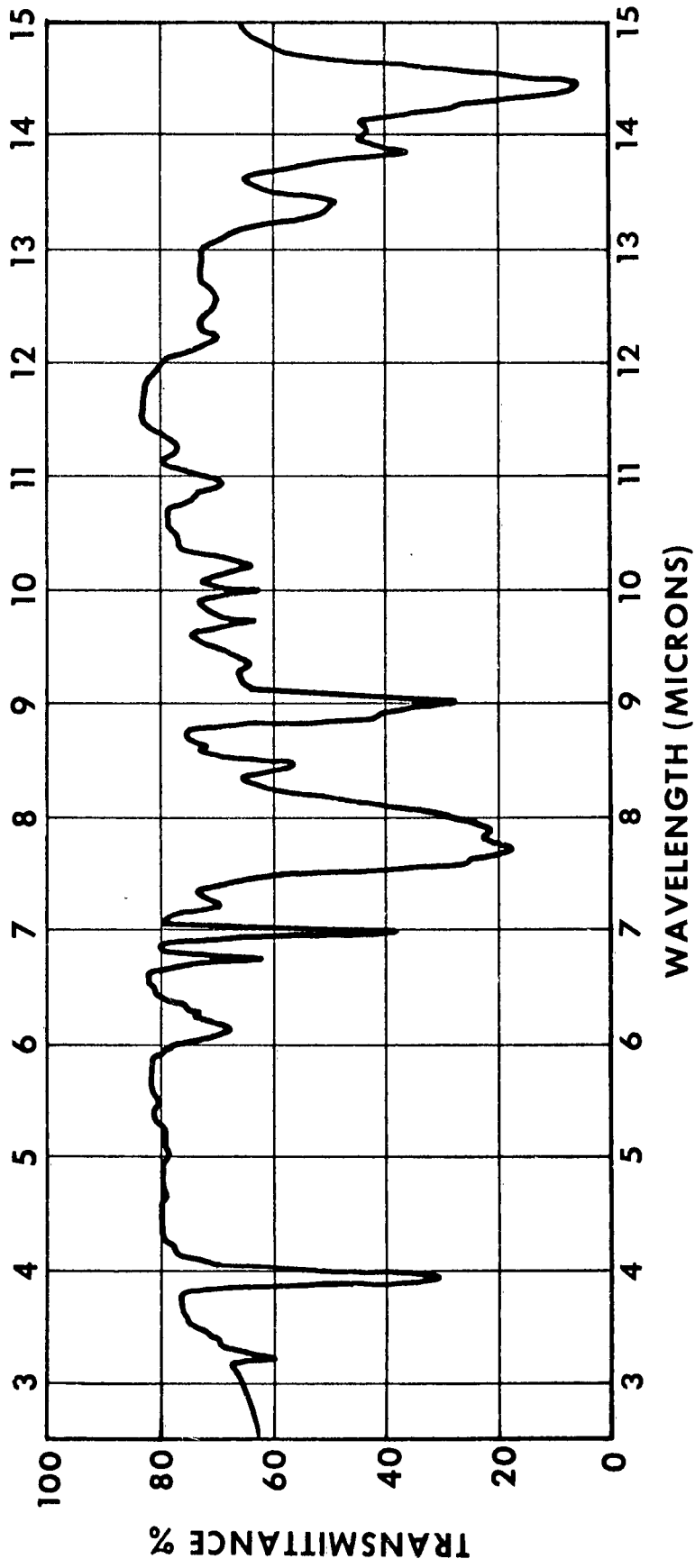


FIGURE 2

INFRARED SPECTRUM OF PYROLYZED PNP II POLYMER (KBr Pellet)

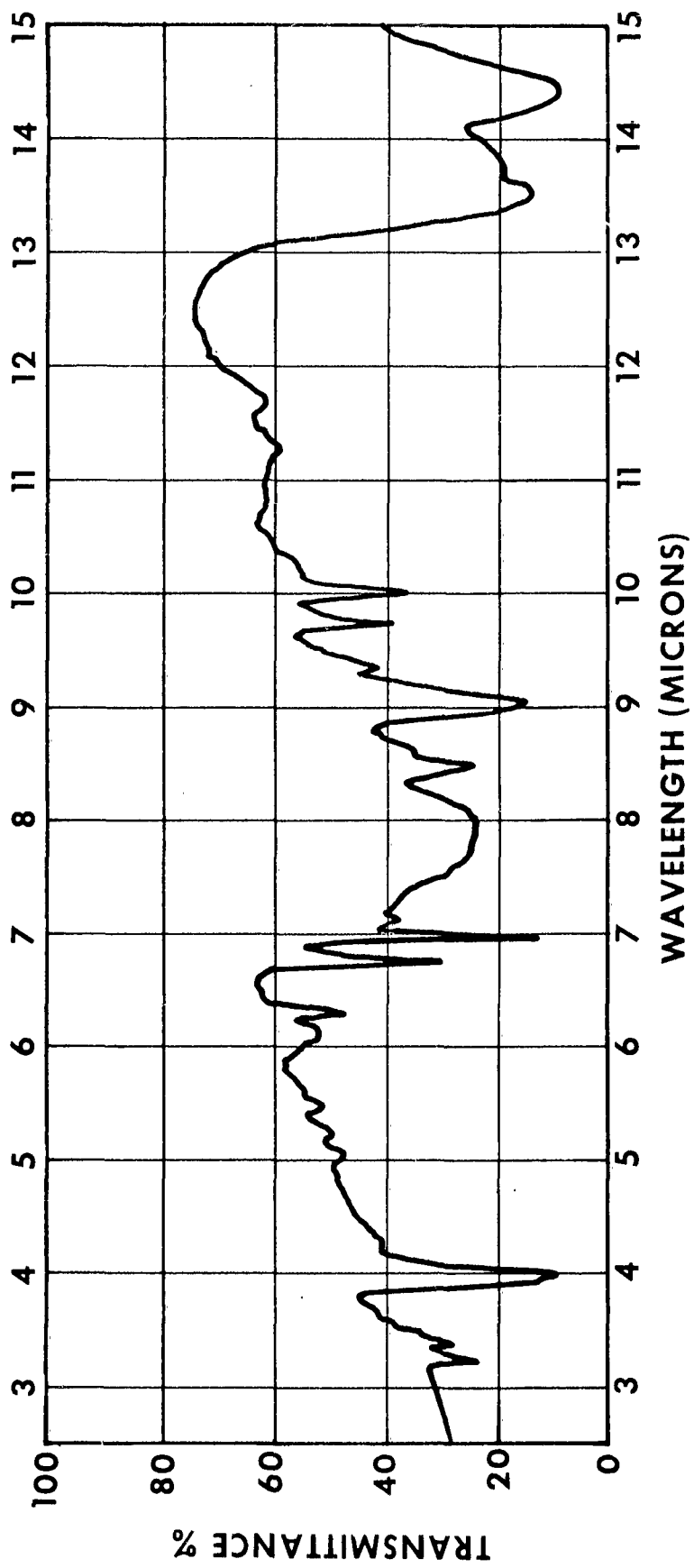


FIGURE 3

INFRARED SPECTRUM OF POP POLYMER (KBr Pellet)

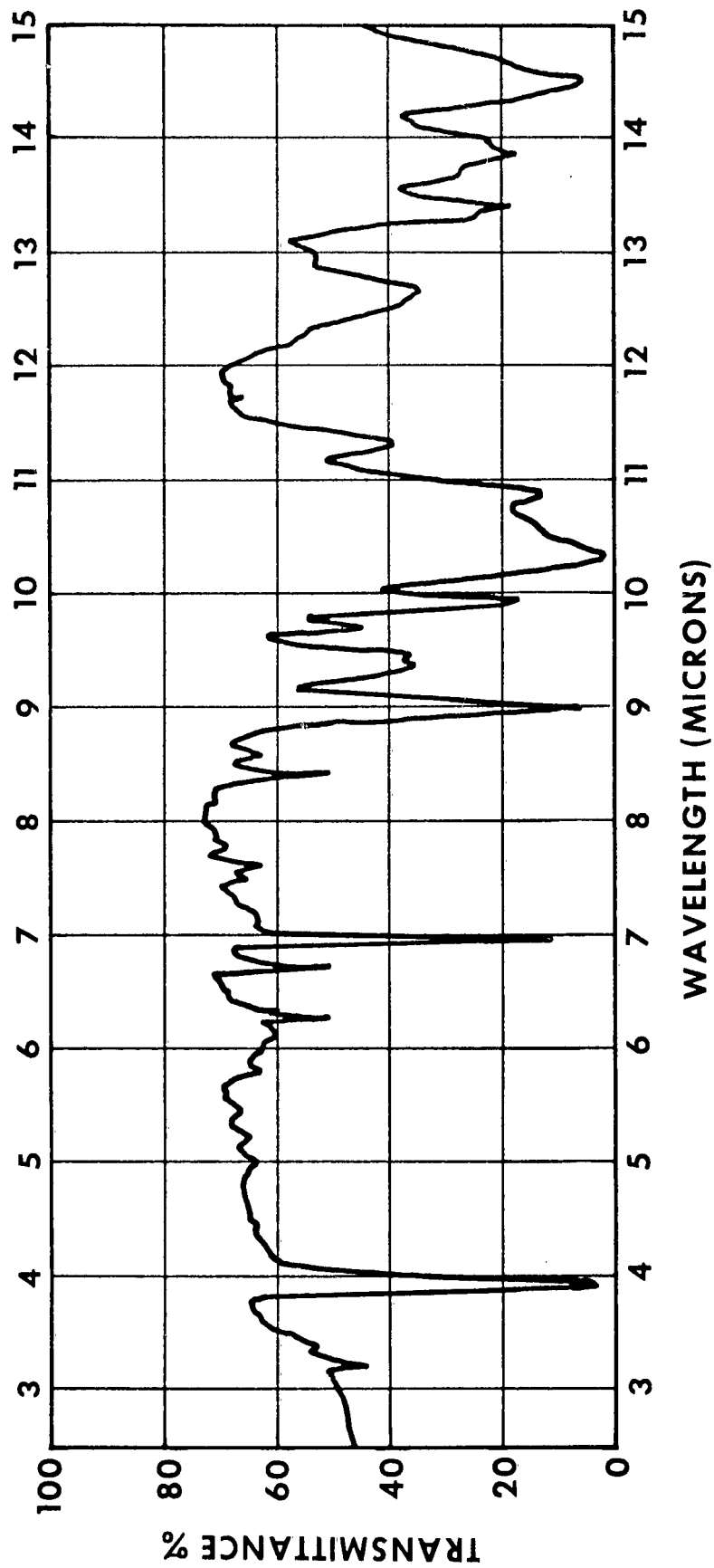
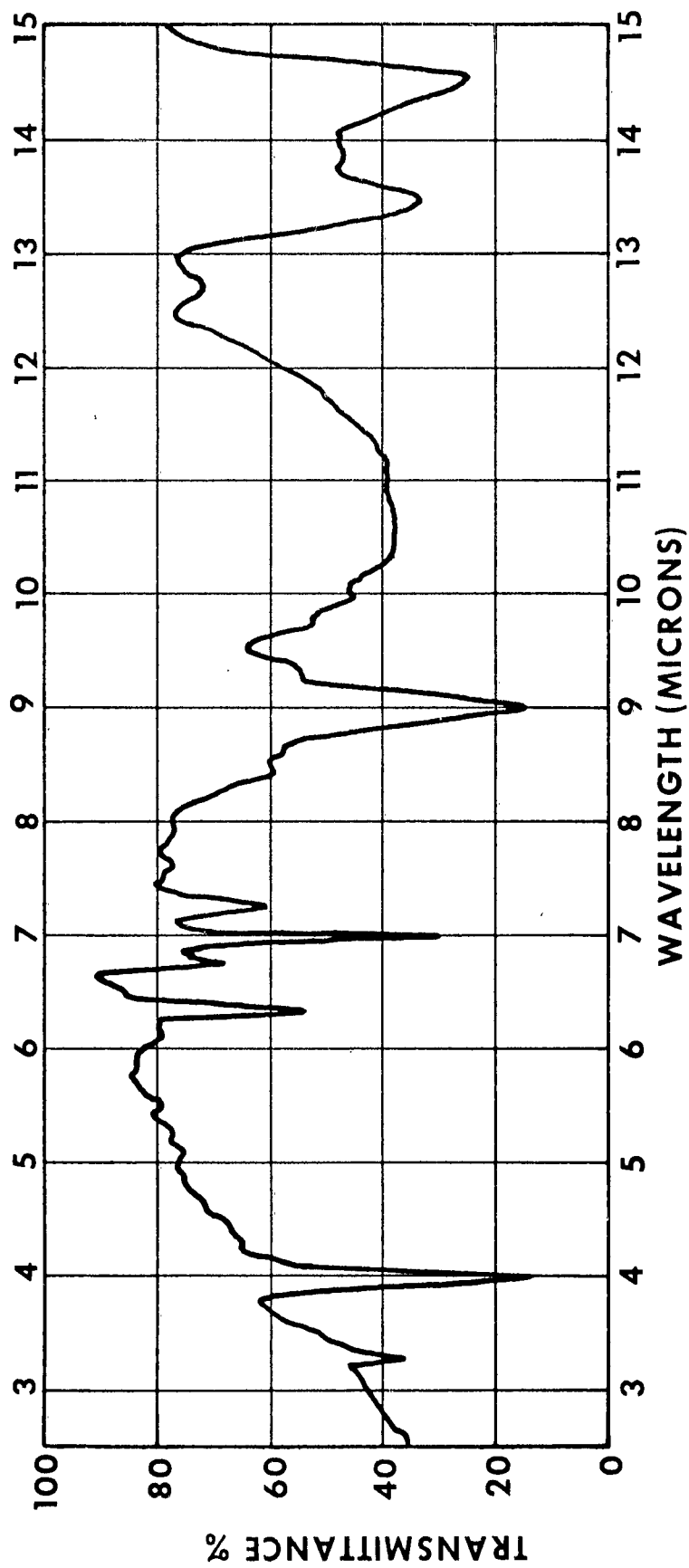


FIGURE 4

INFRARED SPECTRUM OF PYROLYZED POP POLYMER (KBr Pellet)



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