KINETICS OF THE DECOMPOSITION
OF ORGANIC REACTOR COOLANTS

by

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KINETICS OF THE DECOMPOSITION
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INTRODUCTION

The interest in organic fluids as reactor coolants has arisen primarily because of their low vapor pressure at high temperature and their very low corrosiveness. These properties enable the construction of a nuclear reactor without the high pressure piping and expensive corrosion resistant materials that are required with pressuized water cooling.

The main disadvantage of organic coolants is their decomposition under the influence of radiation and high temperature. Early studies showed that polyphenyl-type compounds were the most stable, and considerable work has been done to study the decomposition of these substances. However, much confusion and non-reproducibility of results has arisen because of the wide variety of methods that have been used for creating and measuring decomposition. For example, studies have been made on pyrolytic decomposition, and on radiolytic decomposition by neutrons, gamma rays, and electrons, and usually by combinations of these agents. The amount of decomposition has been reported in terms of change of polymer content, evolution of various gases, changes in viscosity, and changes in infra-red absorption characteristics. Because the correlation among these properties is not well known, it is extremely difficult to predict the rate at which it will be necessary to replace decomposed coolant in a nuclear reactor.

In this study an attempt was made to separate the action of the various destructive influences that are present in a reactor system, and in particular to study the reaction kinetics of the decomposition. The results of this investigation present a method for studying decomposition with a minimum of effort, and clarify the reasons for some of the non-reproducibility that has been previously encountered.

Most of this work is concerned with monoisopropylbiphenyl (MIPB), because, unlike most polyphenyl compounds, it has the added advantage of being liquid at room temperature. The remainder of the studies are primarily concerned with biphenyl and the three terphenyl isomers. Some investigations were also conducted on monomethyl-biphenyl, a compound that is also liquid down to low temperatures.

The presentation of the results has been divided into three main parts, each involving a different type of investigation. The first part concerns radiolytic decomposition by reactor radiation. These data were obtained from irradiations carried out in a facility designed for circulating the organic coolant through a nuclear reactor. The second part concerns radiolytic decomposition by gamma rays. For these experiments the irradiations were conducted in the much simpler manner of exposing test tubes of organic coolant to a cobalt 60 gamma source. In the last part the experiments on the pyrolytic decomposition of organic coolants are discussed. The pyrolysis studies were done in small reaction bombs heated in a carefully controlled oven.

SUMMARY

It was found that all of the polyphenyl compounds investigated polymerize according to a first order rate law under the single influence of reactor radiation or gamma rays or pyrolysis. That is, the rate of polymerization was directly proportional to the amount of remaining unpolymerized material.

When the polyphenyl material was simultaneously undergoing radiolysis and pyrolysis, the situation was found to be more complex. At moderate temperatures, about 200 C to 400 C, the pyrolysis of the polyphenyl was negligible compared to the radiolysis. However, in this temperature range the polymers formed by radiolysis were partially degraded by thermal action. The resulting rate law for poly-merization includes a term for this back reaction. At higher

temperatures, above about 400 C, the pyrolysis became the dominating reaction, and the effects of radiation could be neglected.

It was found that all of the compounds investigated polymerized at almost identical rates under irradiation. However, there were notable differences in pyrolytic polymerization rates between the various polyphenyl compounds. Because pyrolysis is much more important than radiolysis at high temperature, the thermal stability of the coolants was found to be the factor which determines the maximum temperature at which the coolant can be utilized. The relative maximum utilizable temperatures were found for the various compounds that were studied. These compounds in order of decreasing thermal stability are: biphenyl, all three terphenyl isomers, monomethylbiphenyl, and monoisopropylbiphenyl.

These studies also brought out differences in the decomposition products formed by radiolysis and pyrolysis. In general, the products formed during the former process were polymerized to a greater degree than those formed by pyrolysis. The products formed by gamma ray and neutron radiolysis were quite similar. However, certain small differences were found which were interpreted as being the result of the difference in the mode of energy transfer between neutrons and gamma rays with organic matter.

The relative damaging power of neutrons and gamma rays was compared on the basis of the amount of polymerization caused by the absorption of a given amount of energy in the hydrocarbon. Fast neutrons were found to cause about 50 to 200 per cent more polymerization than that caused by the absorption of an equal amount of gamma ray energy.

PART I - RADIOLYTIC DECOMPOSITION BY REACTOR RADIATION

REACTOR RADIATION

In a nuclear reactor there is a variety of types of radiation, all of which may interact to some degree with organic matter. Most of this radiation results directly from the fission process or from fission product decay. According to Glasstone (8, p. 71), a total of about 195 mev of energy is released per fission, and is distributed as follows: kinetic energy of fission fragments, 162 mev; beta decay energy, 5 mev; gamma decay energy, 11 mev; neutrino energy, 11 mev; and neutron energy, 6 mev. The fission fragment energy is almost completely converted to heat within the fuel, and the neutrino energy is carried off without interacting with matter. Because of the low penetrating power of beta rays, much of the beta energy is absorbed in the fuel (in a heterogeneous reactor) and appears as heat. The over-all contribution of beta rays to radiation damage will be quite small (4, p. 11-12).

Another important source of damaging radiation results when gamma rays are given off during the capture of thermalized neutrons by various atoms, and in particular, the hydrogen atom (4, p. 11). The gamma rays from this source and from the fission process will interact with organic matter primarily through the Compton effect (4, p. 10). The gamma ray photon collides elastically with an orbital electron in the organic material, and gives up part of its energy. It is apparent that the gamma rays can be responsible for a significant portion of the radiation damage. It is shown in a later section that the gamma rays were responsible for about 25 per cent of the total radiation damage in the reactor irradiation experiments. The remainder of the damage was found to be due to neutrons.

Neutron Damage

The damage to organic materials by neutrons occurs primarily by the scattering of fast neutrons by hydrogen atoms, which in turn recoil and are ejected as fast-moving protons. These ejected protons can subsequently produce more damage (4, p. 9).

It is interesting to calculate the manner in which the neutron damage depends on neutron energy. This calculation is especially important since the measurement of neutron flux in the irradiation facility was made in the epithermal (0.1 ev to 1 mev) energy region (see section entitled Flux Measurement). As will be shown below, the decomposition rate is primarily influenced by neutrons with energies above the epithermal region. The fast end (greater than about 0.1 mev) of the neutron spectrum will vary from point to point in a reactor (namely near and far from the fuel). Therefore, even if the epithermal flux is the same, the decomposition rate may vary from point to point in a reactor. An attempt has been made to calculate the magnitude of this variation. This calculation is important when it is desired to know how much reliability can be placed on using the data obtained in the in-reactor irradiation experiments to predict the decomposition rate in some other test location or reactor having a different flux spectrum.

In the case of damage to organic compounds by neutrons, it can be assumed that the damage is approximately proportional to the energy absorbed from neutrons by the organic. (3), (17) This is fortunate since this means that secondary modes of energy transfer are unimportant; i. e. , only the primary collision need by considered.

Almost all of the energy transferred to the organic from the fast neutrons is by the process of elastic scattering. [a] When a

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[a] The process is not actually elastic since the hit molecule is disrupted, but the binding energies are small enough so that the neutron hardly knows the difference.

neutron hits an atom of atomic mass number A, a given portion of its energy is transferred by elastic scattering such that:

$$\frac{E_2}{E_1} = \frac{A^2 + 2A \cos \theta + 1}{(A+1)^2} \qquad (8, \text{ p. } 140)$$

where θ is the angle of scattering in the center of mass system. E_1 is the neutron energy before collision and E_2 is the energy after scattering. Because the scattering is essentially isotropic in the center of mass system (8, p. 142); the average energy change is:

$$\overline{\frac{E_2}{E_1}} = \frac{1}{2\pi} \int_0^{2\pi} \frac{A^2 + 2A \cos \theta + 1}{(A+1)^2} d\theta = \frac{A^2 + 1}{(A+1)^2}$$

Therefore, $\quad \overline{\Delta E} = E_1 - E_2 = \dfrac{2A}{(A+1)^2} E_1$

$\overline{\Delta E}$ for hydrogen = .500 E_1, $\quad \overline{\Delta E}$ for carbon = .142 E_1

The number of collisions occurring by neutrons of energy E will be proportional to the flux, $\phi(E)$, of energy E and to the macroscopic cross section, $\Sigma(E)$, at this energy. [a] Therefore, the total rate of energy transfer to a hydrocarbon by neutrons of a given energy is proportional to the quantity:

$$\phi(E)E \left[.500 \, \Sigma_H(E) + .142 \, \Sigma_C(E) \right]$$

(This is the energy transferred to the hydrogen atoms plus the energy transferred to the carbon atoms.)

The above expression will be slightly modified to use microscopic cross sections, σ. [b] A new function $\psi(E)$ will be defined for a hydrocarbon having equal numbers of hydrogen and carbon atoms so

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(a) In this case the total cross section is used, since at high energies it has previously been assumed equal to the scattering cross section.

(b) Macroscopic cross section = (microscopic cross section) x (number of atoms). The reason for this modification is that the rate law for polymerization has been derived so that it takes into account the number of organic molecules present.

that:

$$\psi(E) = .500\, \sigma_H(E) + .142\, \sigma_C(E)$$

The damage rate is proportional to the energy transferred to the hydrocarbon by neutrons of all energies. A damage rate parameter, D, which is directly proportional to the damage rate will be defined by:

$$D = \int_0^\infty \phi(E)\, E\, \psi(E)\, dE \quad \text{(a)}$$

$\psi(E)$ should not be considered constant. During the range of importance it varies considerably (see Figure 1).

There are no measurements of $\phi(E)$ at high energies available in the test facility. However, it is possible to make an estimate of how much D may vary with a change in the neutron spectrum by utilizing data from other reactors. In Figure 2 are illustrated two neutron spectra, one near and one far from the fuel. Both of these high energy spectra have been normalized to the same epithermal flux. As a comparison, D has been calculated from the spectra in Figure 2, assuming an epithermal flux at 1 mev of 1 neutron/cm^2/sec. The integration has been done graphically.

When these two spectra are inserted into the damage equation, D equals 20 near the fuel and 8.3 in the moderated position. The rate of damage near the fuel is therefore 2 1/2 times greater than in the moderated position at the same epithermal flux. It should be noted that the cases taken are purely illustrative, and that spectra in some other reactor may vary considerably from those examined.

(a)The fact that the assumptions used in deriving this equation are invalid for low energies does not much influence the value of this integral since

$$\int_0^{.1\text{ mev}} D(E)\, dE \ll \int_{.1\text{ mev}}^\infty D(E)\, dE$$

$$\psi(E) = .500\,\sigma_H(E) + .142\,\sigma_H(E)$$
CROSS SECTION DATA FROM
BNL 325 (10, p. 56, 78)

FIGURE 1

ψ AS A FUNCTION OF ENERGY

NEUTRON ENERGY (Mev)

$\psi(E)$
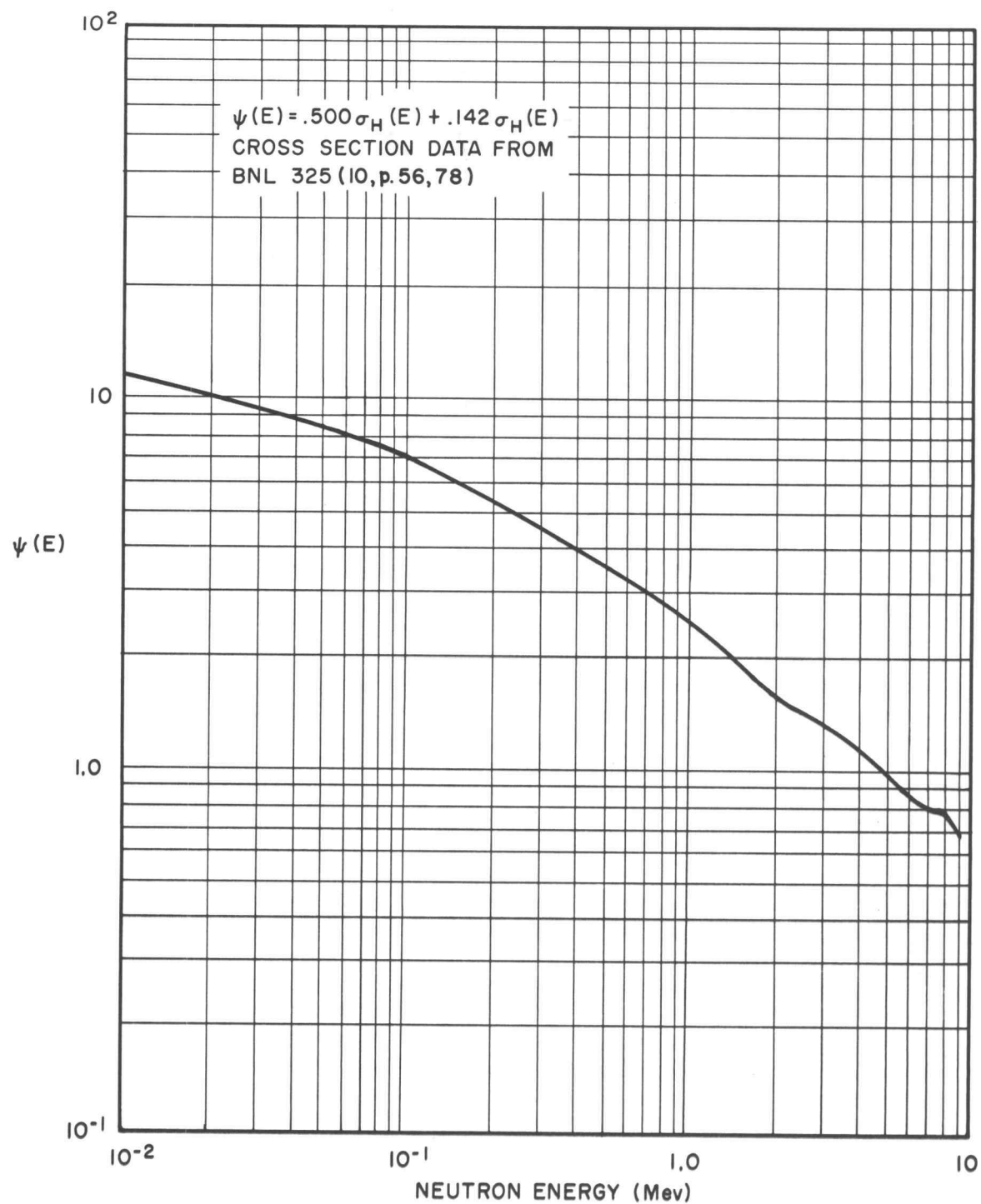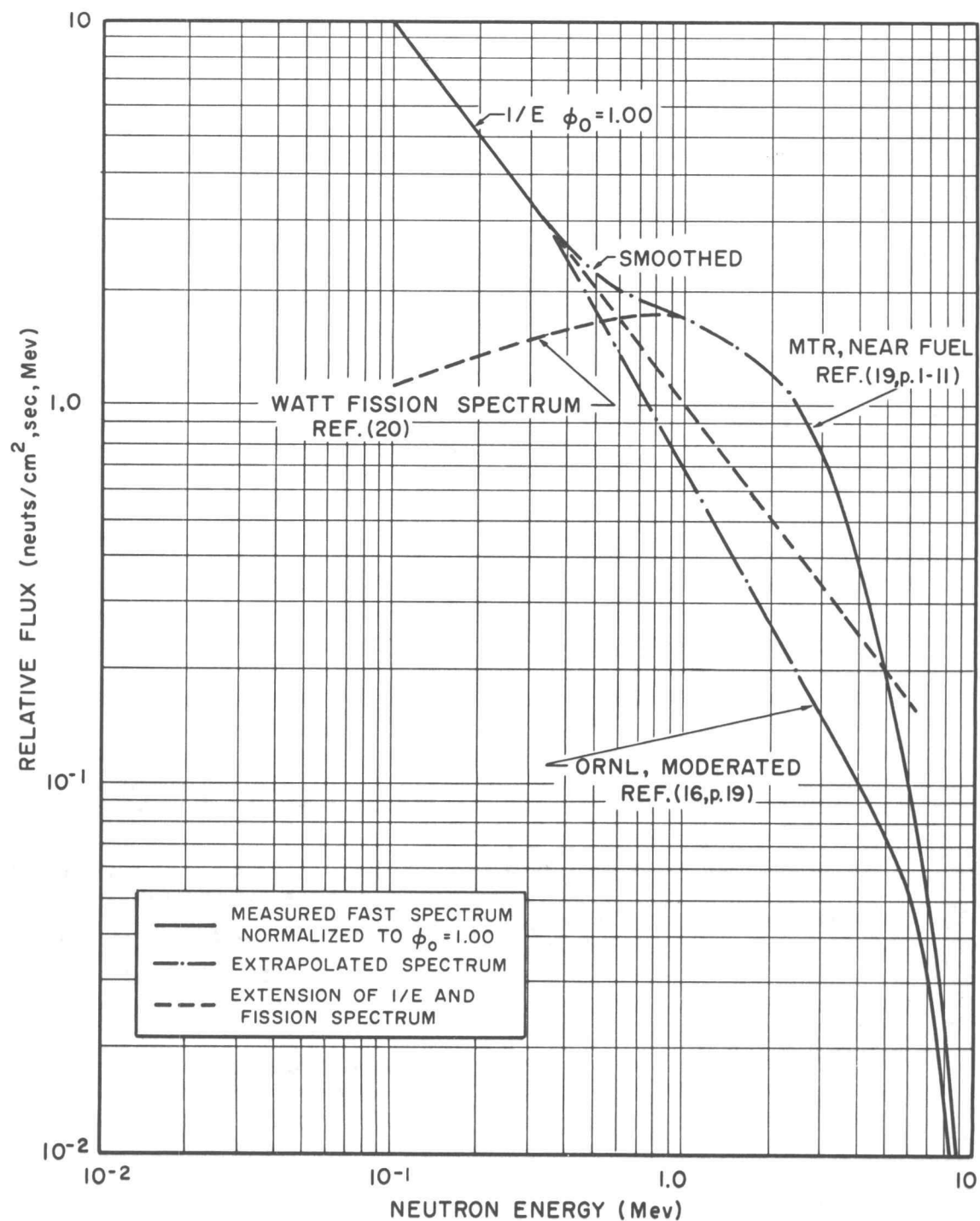
FIGURE 2

REPRESENTATIVE NEUTRON FLUX SPECTRA

The decomposition data reported in this paper were obtained in a position between fuel columns. The fast flux spectrum should resemble that of the moderated type illustrated in Figure 2.

The point that has been made is that it may be inaccurate to extrapolate damage rate data from one irradiation location to another unless the high energy end of the spectrum is known in both locations.

During the graphical integration for the values of D, it was found that the damage at energies less than a few tenths of a mev was negligible. In order to illustrate this relationship in a clear manner, the values obtained by graphical integration above a given energy, E, are presented in Figure 3. The values are given in the form:

$$F(E) = \frac{\int_{E}^{\infty} \phi(E) \ E \ \psi(E) \ dE}{D}$$

so that F(E) represents the fraction of total energy occurring above energy, E. It is seen that essentially all of the neutron damage results from neutrons with an energy in excess of 0.1 mev with any typical flux spectrum. It is also noted that the very fast neutrons, with energies in excess of about 3 mev, (of which there are relatively few; see Figure 2) cause a significant portion of the damage.

OPERATION AND DESCRIPTION OF THE IRRADIATION FACILITY

Test Objectives

In order to study the various effects of radiation and temperature on the decomposition of organic coolants, these two subjects were investigated separately. The coolants were irradiated at a relatively low temperature so that irradiated organics were obtained that had undergone essentially no pyrolytic damage.
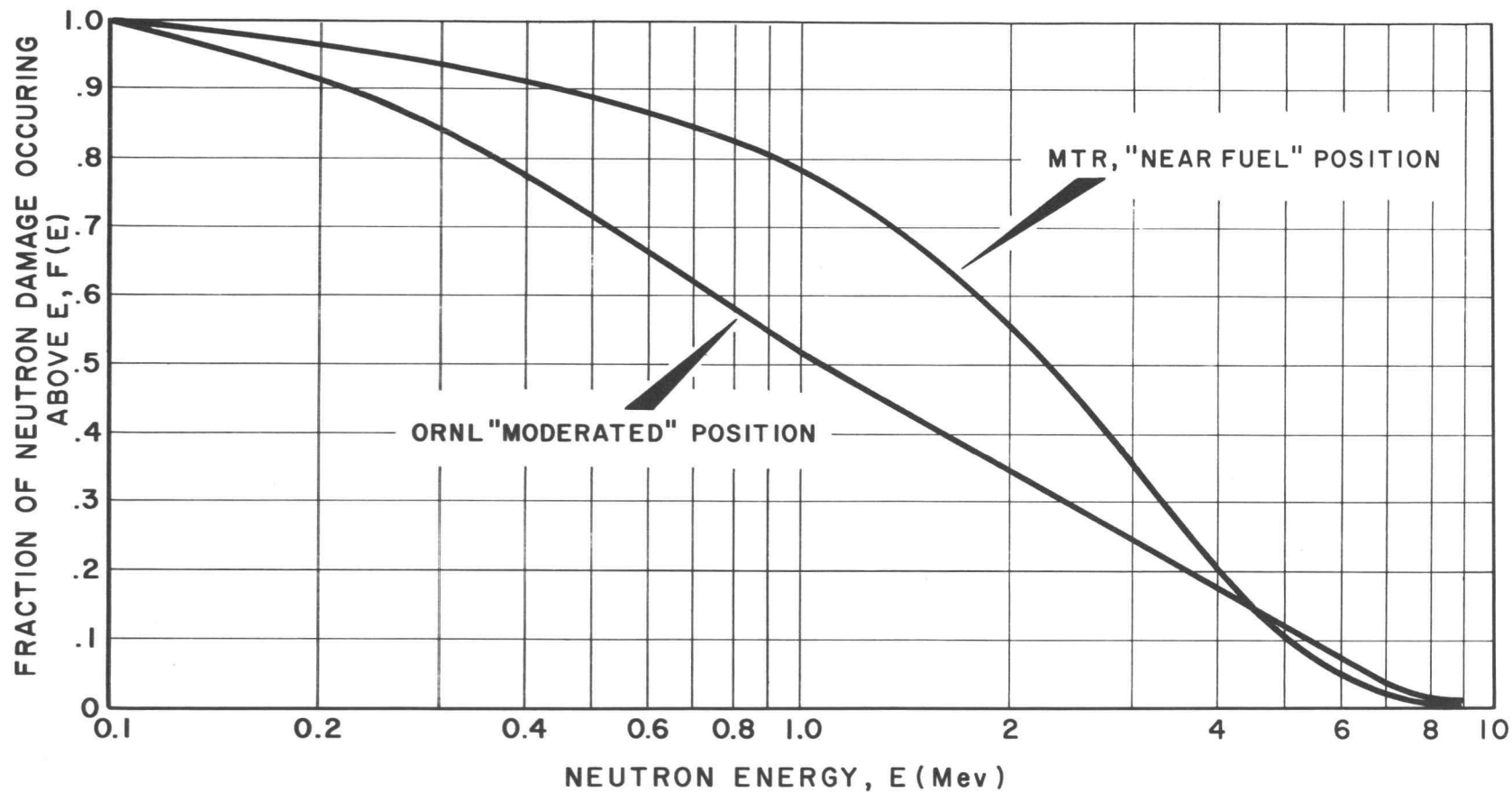
FIGURE 3

NEUTRON DAMAGE AS A FUNCTION OF ENERGY

Experiments were later conducted on heating these irradiated organic coolants and on heating unirradiated organics. The comparison of the changes that occurred provide valuable insight into the mechanisms of radiolytic and pyrolytic damage.

All of the in-reactor testing was conducted with organic compounds that were liquid near room temperature.

MIPB and a low melting biphenyl-terphenyl eutectic were the two coolants that were irradiated. Both of these coolants have previously been irradiated in tests in the Brookhaven reactor (11), (12). A mixture of MIPB and terphenyls was also irradiated, but only to serve as a check on the decomposition rate measurements, not because of its possible use as a reactor coolant.

Operational Procedure

The organic coolant was irradiated in the reactor by pumping it through the flux zone by means of a simple flow loop arrangement. A schematic flow diagram of the loop is shown in Figure 4. The out-of-reactor components of the loop were constructed of stainless steel and consisted principally of a storage tank containing cooling coils to remove the gamma heat, and a "Chempump" to circulate the fluid. The total liquid volume of the system could be varied between about 20 and 35 gallons. During the experimental runs the flow varied from about 6 to 14 gallons per minute. All of the free space in the loop was blanketed with helium or nitrogen gas. [a]

The portion of the loop external to the reactor was surrounded by a shield of lead bricks. Because of the large volume of radioactive coolant [b] in the storage tank it was only permissible to go inside of the lead shield for about five minutes at a time (per day per man).

(a) Helium was used only in the run with MIPB.

(b) The radioactivity was mainly due to the activation of chlorine which was present as an impurity.
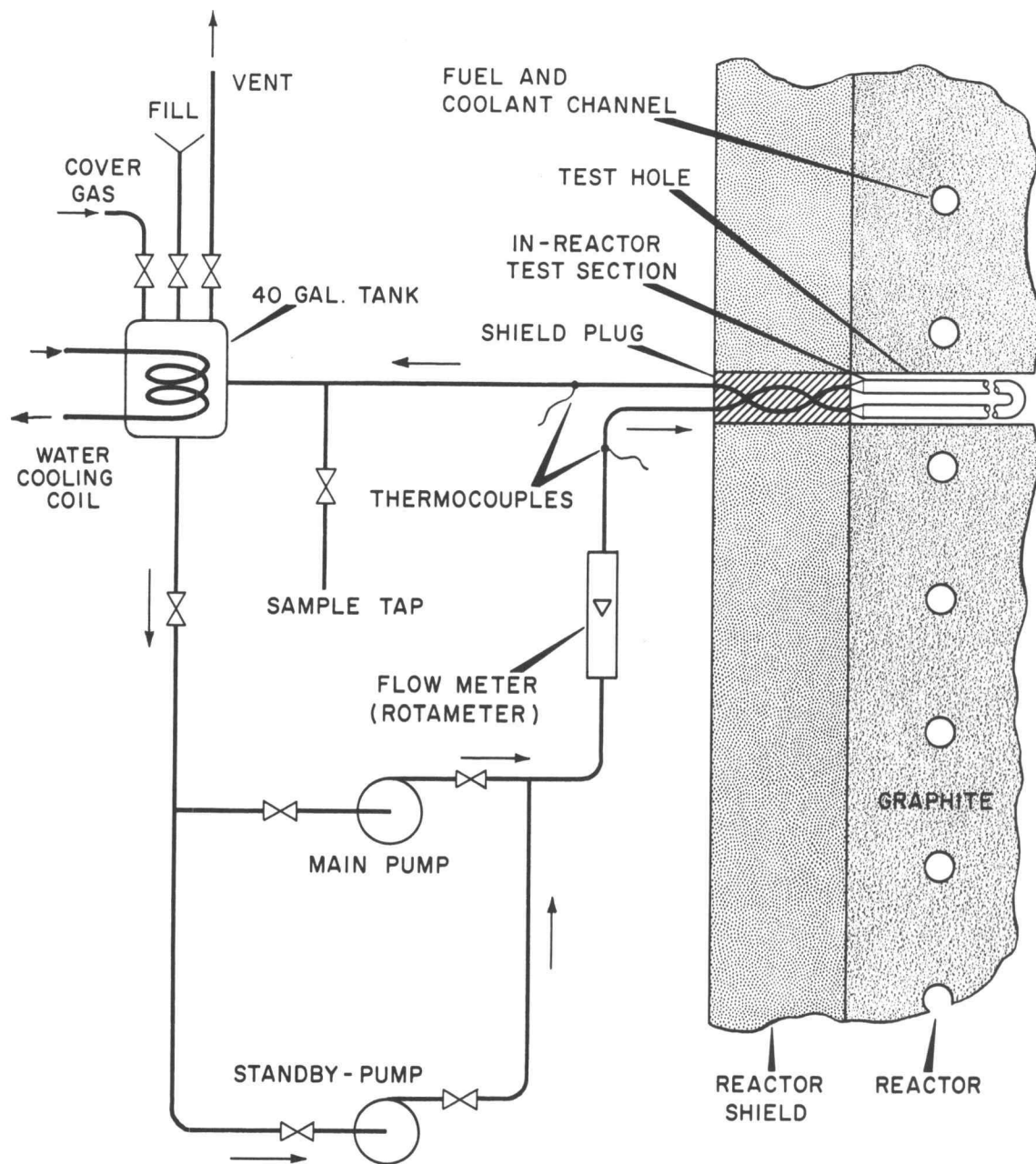
FIGURE 4

SCHEMATIC FLOW DIAGRAM OF IN-REACTOR
TEST FACILITY

The portion of the loop located within the flux zone of the reactor consisted of two adjacent aluminum tubes (inlet and return). A segment of this section is illustrated in Figure 5. The total volume of organic coolant in the flux zone was 4.4 gallons. This in-reactor test section was connected to the external piping by means of two 1/2 inch tubes that were spiraled through the shield plug in such a manner that neutrons could not stream out of the reactor.

Samples of the irradiated coolant could be drawn at any time during loop operation, so that a continuous record of composition changes could be maintained. The sample line was extended beyond the lead shield so that the radiation dose rate at the sample tap was quite low.

The practice during the runs was to irradiate the coolant until its viscosity became so great that pumping difficulty was experienced. At this time a fraction of the loop contents were drained and fresh coolant was added. This process, irradiating then diluting, is designated as an operational "cycle".

All of the cycles with MIPB were of sufficient length so that reliable decomposition data were obtained. At the time the eutectic mixture was first irradiated pump trouble was experienced, with the result that frequent dilutions of the irradiated eutectic were necessary in order to decrease the coolant viscosity. These runs furnished very little decomposition rate data, but two subsequent cycles to high exposure were successful. The decomposition data reported on the eutectic is from these two extended runs. The MIPB-terphenyl mixture was irradiated successfully through two cycles.

The temperature at which the irradiations were conducted was maintained between 80 and 100 C. All of the heating was supplied by gamma and neutron absorption in the in-reactor assembly. At this temperature the rate of pyrolytic damage to the pure compounds studied is essentially zero. As will be brought out later (See section entitled
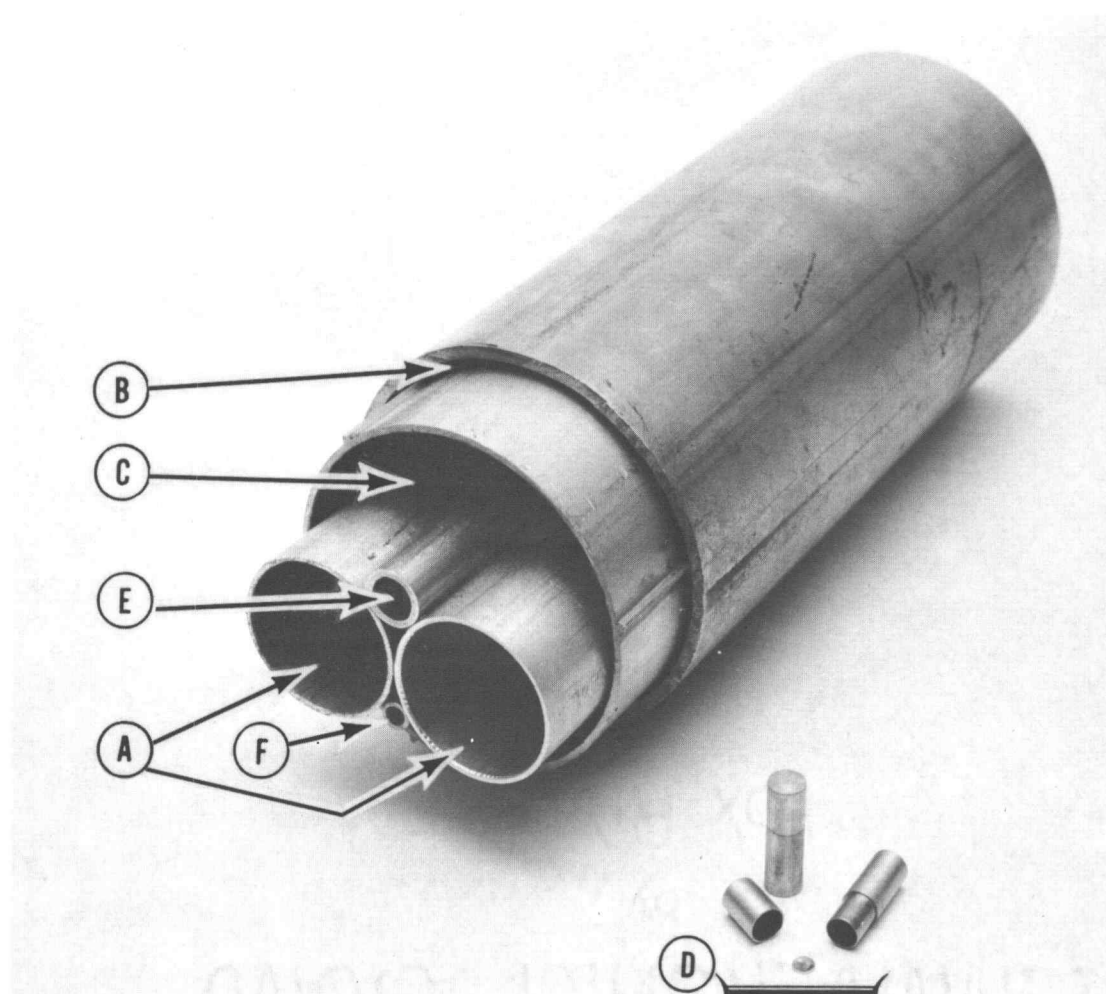
A. INLET AND RETURN TUBES FOR ORGANIC COOLANT

B. WATER COOLANT ANNULUS TO PREVENT OVERHEATING OF SECTION.

C. DEAD GAS SPACE.

D. COBALT-ALUMINUM ALLOY FOIL WITH MAGNESIUM AND CADMIUM CAPSULES USED TO HOLD FOILS.

E. PNEUMATIC TUBE USED TO INTRODUCE FOIL CAPSULES IN REACTOR.

F. AIR SUPPLY LINE TO FAR END OF PNEUMATIC TUBE FOR BLOWING CAPSULES OUT OF REACTOR.

FIGURE 5

IN-REACTOR LOOP SECTION

Combined Radiolytic and Pyrolytic Decomposition), the pyrolytic poly-
merization rate of the coolant does not approach a typical radiolytic
rate until the temperature is around 400 C. For this reason the poly-
merization rates observed during these experiments can be considered
to result entirely from radiolytic action.

Flux Measurement

The neutron flux in the in-reactor test section was monitored
by inserting bare cobalt (aluminum alloy) foils into the flux zone. The
tubing through which the foils were inserted and the transport capsules
can be seen in the illustration of the in-reactor test section (Figure 5).
These foils were counted for cobalt 60 activity after discharge and the
thermal neutron flux was calculated. The epithermal flux was calcu-
lated by means of cadmium ratio measurements (9). In this procedure
some of the cobalt is irradiated in cadmium capsules so that the cobalt
is only activated by neutrons in the epithermal energy range. [a] This
flux calculation gives rise to a "ϕ_O" term, where for an epithermal
flux varying inversely as the energy, E:

$$\text{Epithermal neutrons/cm}^2, \text{sec} = \frac{\phi_O}{E \text{ (mev)}}$$

All exposures have been reported in terms of this ϕ_O term.
The simplest manner in which to consider this term is as the value of
the flux at 1 mev.

The neutron flux along the in-reactor test section was averaged
taking into account variation in flux intensity along the length of the
section. Thus, the reported exposures are an average over the entire
4.4 gallons of coolant in the flux.

The gamma flux in the reactor also contributes toward the
decomposition of the organic. The gamma exposures were calculated
from corrected heat generation measurements in aluminum made
under a similar geometrical arrangement to the test section. During an

(a) Cadmium captures most of the neutrons below an energy of about
0.5 ev.

integrated epithermal, ϕ_o, exposure of 10^{18} neutrons/cm^2, the gamma exposure was 8 x 10^9 Roentgens.

ORGANIC COOLANT COMPOSITION

The MIPB was obtained from the Monsanto Chemical Company, and was irradiated without further purification. The approximate isomeric composition of the material is 62 per cent meta- and 38 per cent para-isopropylbiphenyl. The pour point is -55 C, and the normal boiling point ranges from 295 to 300 C.

The eutectic was prepared by mixing together commercial grade terphenyls[a] and biphenyl; in the proportions of 55 per cent ortho-, 20 per cent meta-terphenyl, and 25 per cent biphenyl. The resulting mixture contained, as an impurity, about 0.1 per cent para-terphenyl which initiated the formation of large amounts of crystals containing all the para-terphenyl and a fair amount of the other constituents.[b] These crystals caused the mixture to be of a mushy nature until heated to 30 to 40 C. In order to produce a completely liquid eutectic the mixture was melted, then cooled until crystals just started to form, and then filtered. The filtrate contained essentially no para-terphenyl, and had a pour point of about -15 C.

A mixture of MIPB and terphenyls was utilized in one test. This was made up by mixing together 40 per cent MIPB, 40 per cent ortho-terphenyl, and 20 per cent meta-terphenyl. About three per cent of para-terphenyl was present as an impurity. This mixture contained some crystals at temperatures below 50 C, but it was sufficiently fluid at room temperature to permit operation of the loop.

DECOMPOSITION OF THE COOLANTS

Analyses of Samples

In order to examine such quantities as decomposition rates, it

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(a) Santowaxes O and M, manufactured by Monsanto Chemical Company
(b) The para-terphenyl content of the crystals was about six per cent

is first necessary to have some index of decomposition. When the organic compounds are decomposed they produce liquid and gaseous products with a wide range of volatility. The proportion in which these products are formed is sensitive to the experimental conditions (this factor will be brought out later and is one reason why it is difficult to correlate the results of some experiments with others).

Most of the mass of the decomposition products exists in the form of tar (high boiling polymers). Because the tars are the products that most influence the physical properties of the coolants, the formation of tars is the most interesting subject to investigate.

The tar content was determined by a single plate distillation under reduced pressure. The distillation method was an adaption of a procedure for determining tars developed by R.H.J. Gercke of Atomics International. Good separation between the polymers and the pure organic coolant was obtained. All of the samples were distilled for 1 1/2 hours under the conditions of temperature and pressure listed in Table 1. The amount of tar was determined by weighing the distilling flask before and after distillation. It is shown later that the radiolytic tars may partially decompose under the distillation conditions. However, the loss of degradation products is less under distillation conditions than under reflux since the residue reached constant weight in about an hour. (Compare with Figure 13.) The error introduced by this effect should only be on the order of two per cent.

TABLE 1

Temperature and Pressure Conditions for Distillation

Material	Temperature, °C	Pressure, mm of Hg
Monoisopropylbiphenyl	175	10
Monomethylbiphenyl	178	30
Biphenyl	187	25
Ortho-terphenyl	185	2.5
Meta-terphenyl	185	2.5
Para-terphenyl	215	2.5

Some of the above compounds were used only in the pyrolytic decomposition tests. The same procedure for determining tar content was used throughout the experiments on radiolytic decomposition by reactor radiations and by gamma radiation, and in the experiments on pyrolytic decomposition.

In addition to the tars, there were a fair amount of liquid products formed with boiling points below that of the pure compound. It was found, however, that these low boiling products polymerized at about the same rate as the pure undecomposed compound (See section entitled Rate of Radiolytic Polymerization). For this reason the most meaningful results were obtained when the pure compound and the low boiling compounds were considered together as unpolymerized coolant, and equal to the fraction that was not tar.

Infra-red absorption techniques were used to determine the biphenyl and terphenyl content of the irradiated eutectic. In this procedure the eutectic was first separated from the tar by distillation and then infra-red absorption measurements for biphenyl and the two terphenyls were made on the eutectic. Results of an apparently spurious nature were occasionally obtained, supposedly due to incomplete distillation of the eutectic from the tar.

Some of the preliminary infra-red measurements that were reported in earlier versions of this work were in error. In those measurements the amounts of ortho- and meta-terphenyls were determined by the infra-red absorption of the irradiated eutectic while it still contained polymer. The biphenyl was calculated as making up the unaccounted for portion of the samples. It was later found that some of the decomposition products absorbed in the same bands as the terphenyls. [a] This produced high concentration values for the terphenyls and consequently, low concentrations for the biphenyl.

(a) 12.36 microns for meta-terphenyl and 12.80 microns for para-terphenyl.

In one experiment MIPB was mixed with ortho- and meta-terphenyl and then irradiated. In order to analyze these samples the high boiling decomposition products were first separated by distillation, and the amount of MIPB in the distillate was measured by infrared absorption (at 3.40 microns). The amount of terphenyls in the distillate could not be determined since part of the low boiling MIPB decomposition products absorb in the same region as the terphenyls.

Polymerization of the Coolant

The composition of the irradiated coolant was not determined in the sense of actually identifying all of the compounds formed. Actual identification is a major project, although studies of this type have been undertaken, notably at California Research Corporation and at Atomics International. There are, however, certain easily obtained physical property measurements that can be made, which indicate the degree of polymerization of the irradiated coolant. Viscosity is very sensitive to molecular weight and to the shape of the molecule. [a] If two samples of irradiated organic coolant contain the same amount of tar, but their viscosity differs, the sample having the highest viscosity will contain the highest molecular weight tars. (This statement includes the inherent assumption that the polymerization follows through some sequence resembling a homologous series.) Thus, plots of tar content versus viscosity yield insight into the changes in tar composition during irradiation.

The examination of the changes in polymerization brought on by heating the coolant lead to an explanation of the results that are observed when the coolant is simultaneously irradiated and heated.

Effect of Cycling on Composition of the MIPB

Cycling is a term used here to describe the process of removing part of the irradiated coolant from the loop and replacing it with

(a) High molecular weights, or long polymers, increase the viscosity.

pure coolant, then continuing the irradiation. In the run with MIPB, there was a large number of cycles, so that changes in polymerization with cycling could be investigated. There were not enough cycles in the eutectic test to examine this point.

As the MIPB is cycled, the viscosity of the coolant increases, even though the tar content is the same as that in the previous cycle. This effect is illustrated in Figures 6 through 9. The viscosity increase indicates that the tar remaining from the previous cycle is undergoing further polymerization. This process continues until a point is reached where a steady state composition is attained and the viscosity no longer increases (for a given tar concentration). During the tests there is very little change in viscosity after the fourth cycle and none detectable after the sixth.

The change in the concentration of low molecular weight compounds during cycling can be conveniently examined by distillation. Again it is assumed that the low boiling compounds form a more or less homologous series so that an increase in boiling point can be taken to show an increase in molecular weight. Figure 10 shows the distillation curves for samples from the first and fifth cycles. The concentration of compounds with a boiling point around that of biphenyl increases with cycling. Biphenyl has been identified as making up at least part of this component.

The following description is one interpretation of the above observations. As the MIPB is irradiated it forms polymers and a smaller fraction of low boiling compounds. Upon continued irradiation some of the polymers undergo further radiolytic polymerization. By these processes both the average degree of polymerization of the tar and the amount of low boiling compounds would be increased during cycling in the manner that was observed. The low boiling compounds may also be polymerized by radiation, in which case some steady state concentration of lighter products will be reached. The cycling data
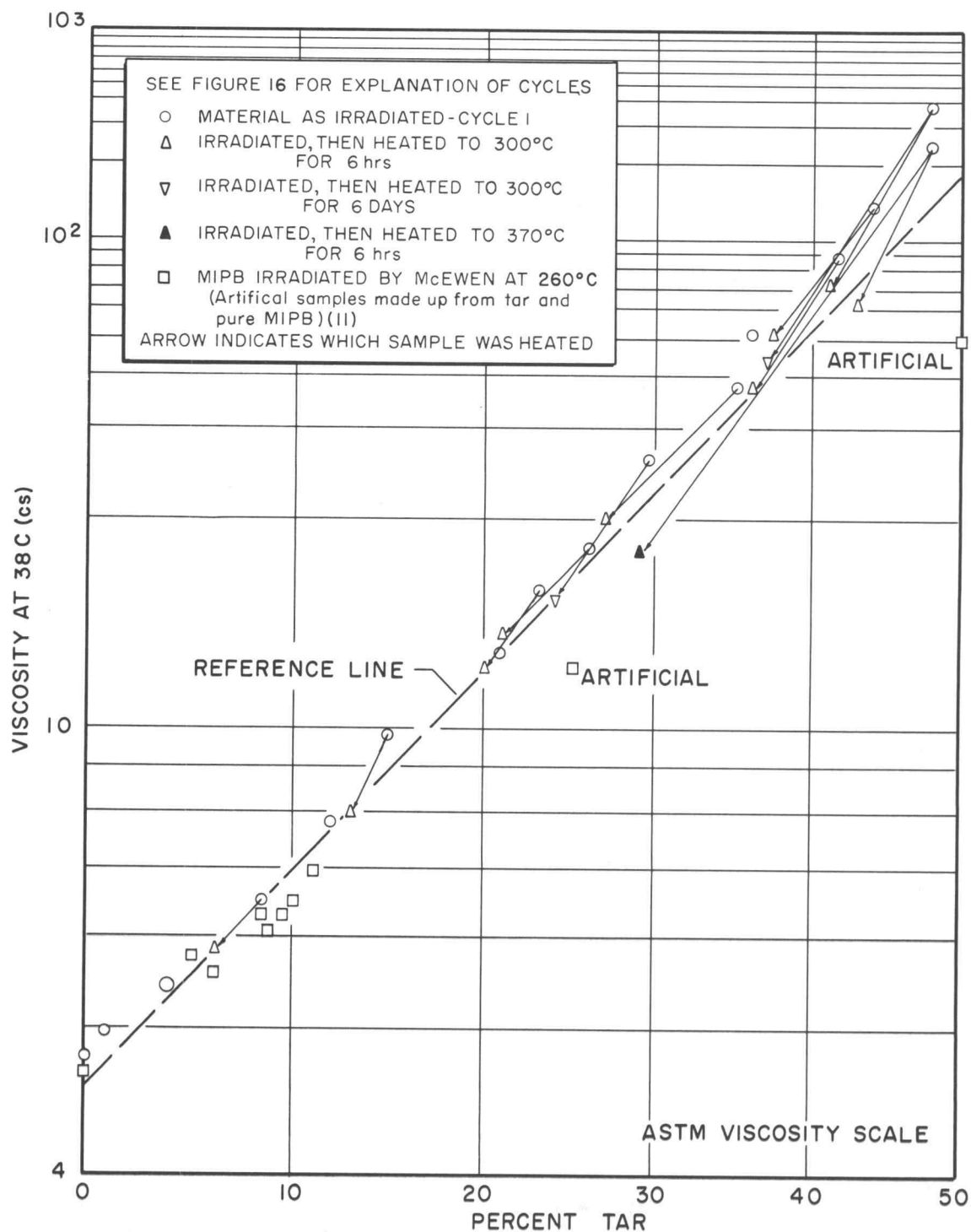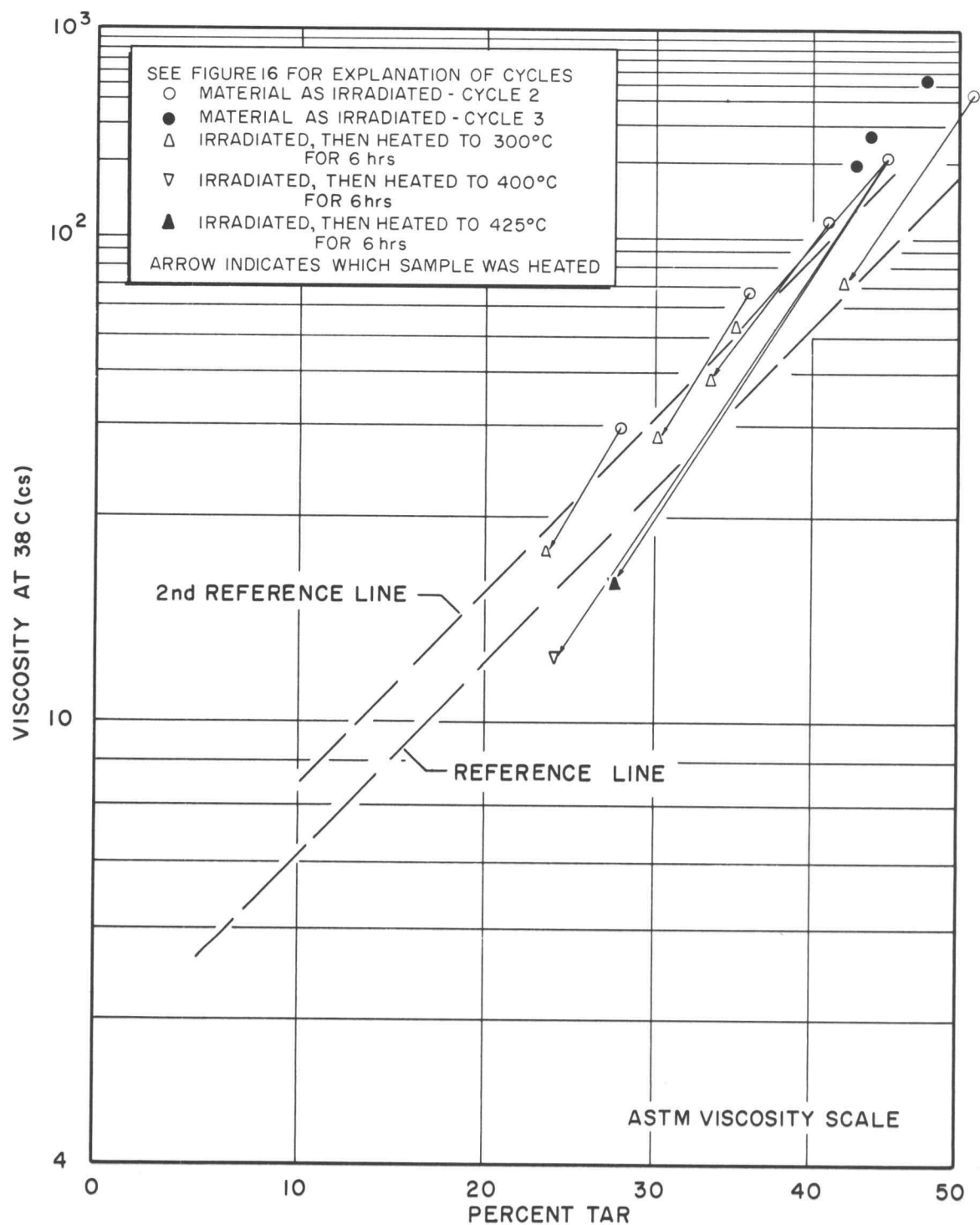
FIGURE   6
VISCOSITY OF IRRADIATED MIPB
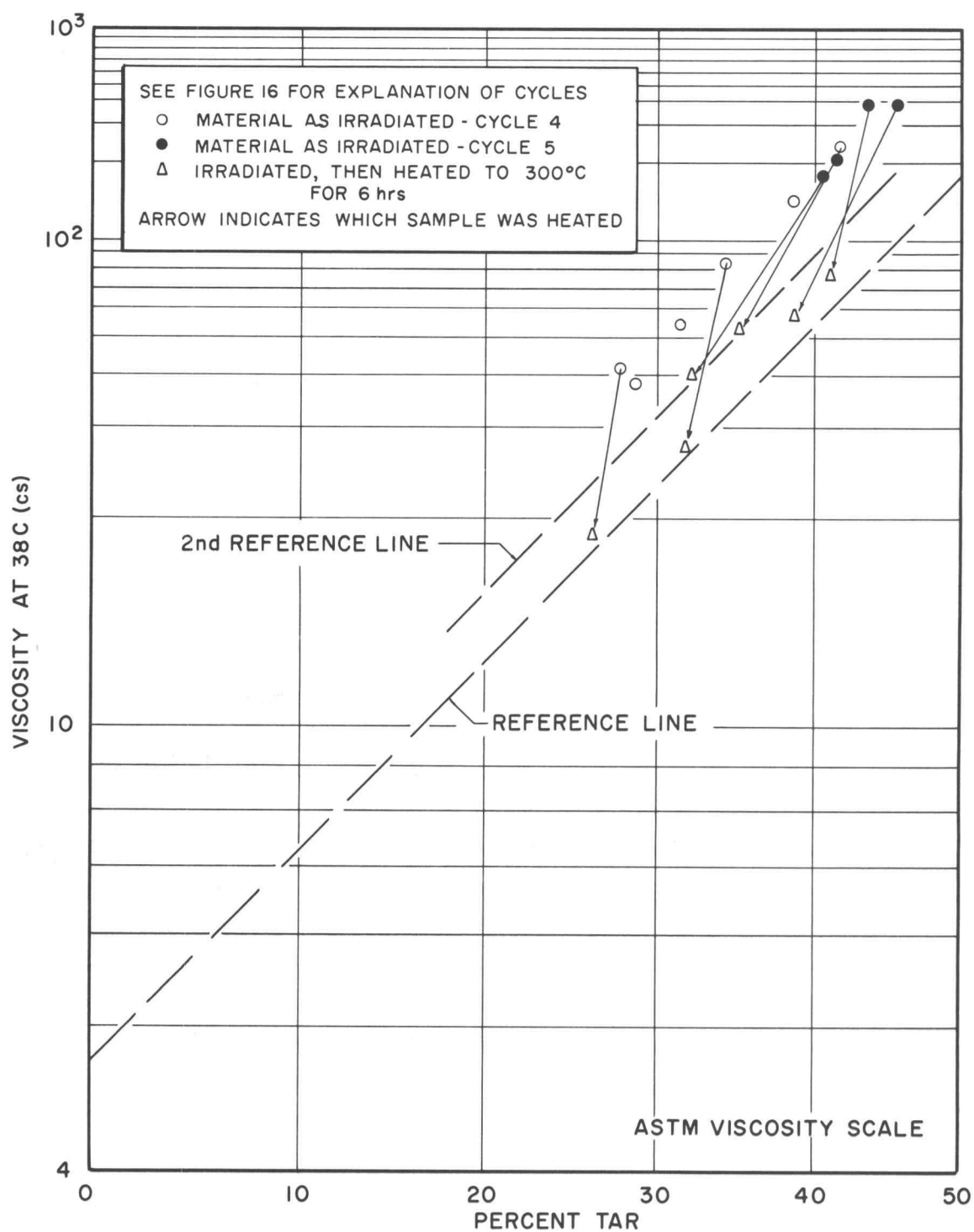
FIGURE 7
VISCOSITY OF IRRADIATED MIPB

FIGURE 8
VISCOSITY OF IRRADIATED MIPB
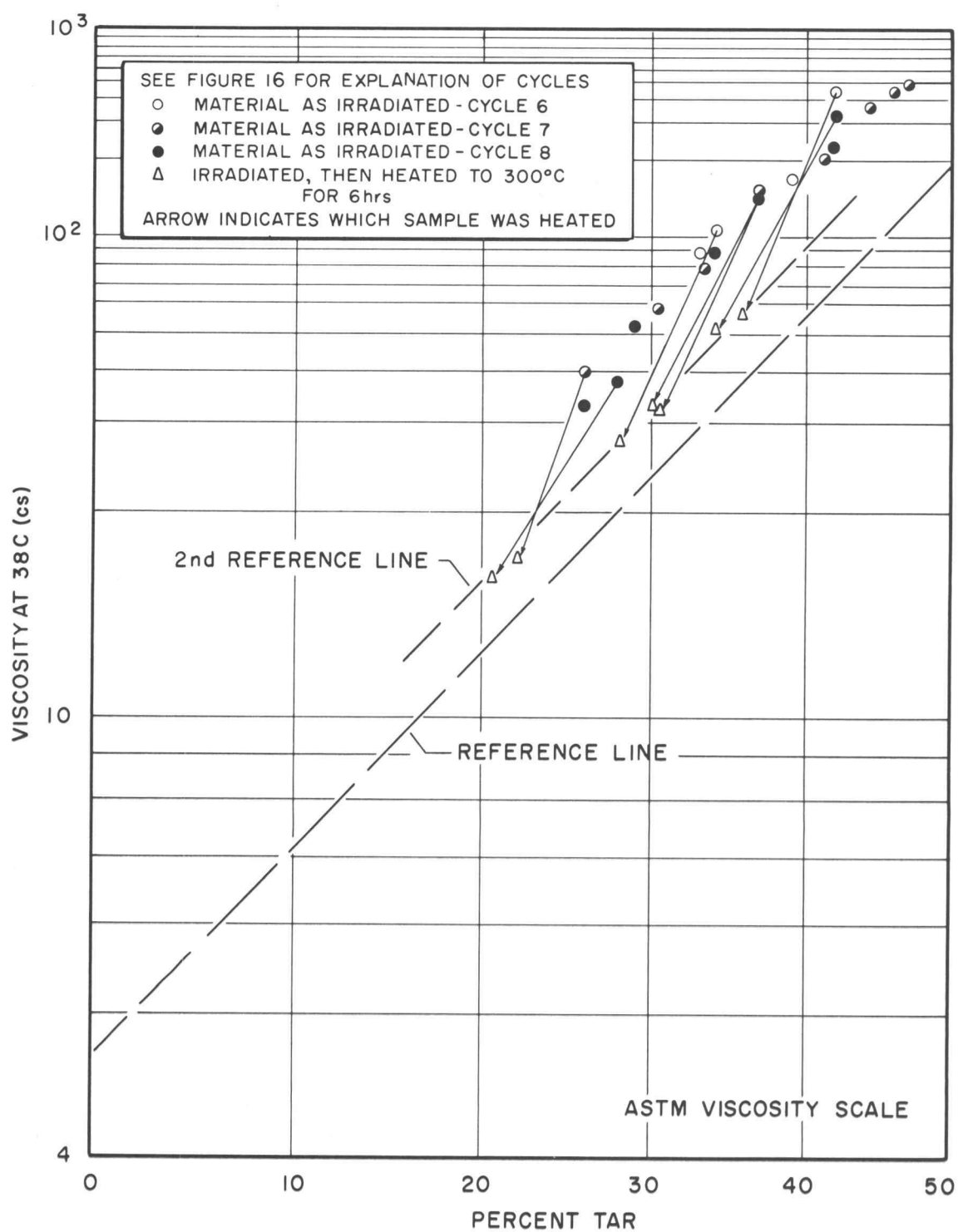
FIGURE 9
VISCOSITY OF IRRADIATED MIPB

are not extensive enough to examine this last hypothesis, however, the decomposition rate data presented later show that this must be the case.

Effect of Temperature on the Irradiated MIPB

Some of the samples that were irradiated were subsequently heated in various manners to investigate the effect of temperature on the irradiated coolant. Most of the heating was done by refluxing the irradiated material under a helium atmosphere. All of these samples are reported as being heated at 300 C, although the reflux temperatures actually varied between 295 and 300 C. Samples that were to be heated above 300 C were placed inside of glass liners, sealed into helium filled bombs, and then heated in an oven. This is the same experimental procedure that was used in the pyrolysis studies.

As has been previously pointed out, the MIPB was irradiated at a temperature below 100 C. When this irradiated MIPB was subsequently heated to temperatures in excess of about 120 C, changes in its composition occurred. The heating caused a degradation of the polymers with a resulting decrease in both tar content and in viscosity. This effect is illustrated in Figures 6 through 9.

The change in viscosity and tar content shows that the radiolytic polymer is less stable towards pyrolytic damage than is the MIPB (MIPB decomposes only very slowly at temperatures below 400 C). Figure 11 shows the change in the low boiling components that occurs with heating the irradiated MIPB. The fraction of MIPB remains essentially constant, but the fraction with the boiling point near biphenyl (probably mostly biphenyl) increases. This indicates that low boiling fragments break off the polymers during degradation. In addition, some gas is formed during heating.

Figure 12 shows that the composition starts to change noticeably at about 120 C.[a] Figure 13 indicates that the pyrolytic destruction

(a) Some experiments have shown that if the initial viscosity is much lower (10 to 20 cs) the change is not noticeable until the irradiated material is heated to about 250 C.
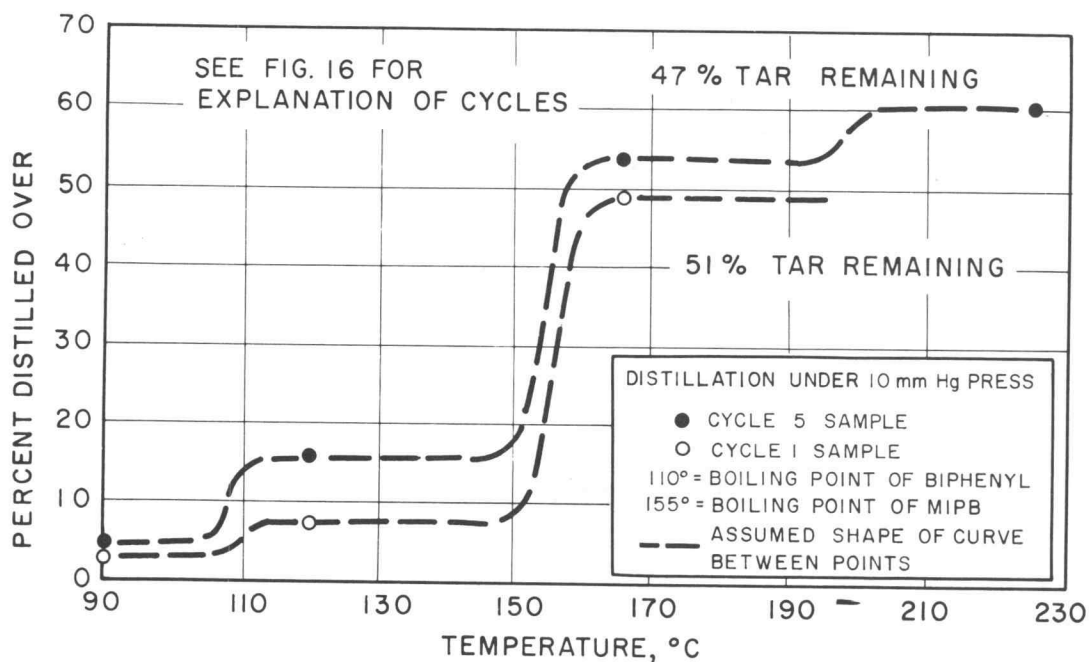
FIGURE 10

CHANGE IN COMPOSITION OF IRRADIATED MIPB WITH CYCLING
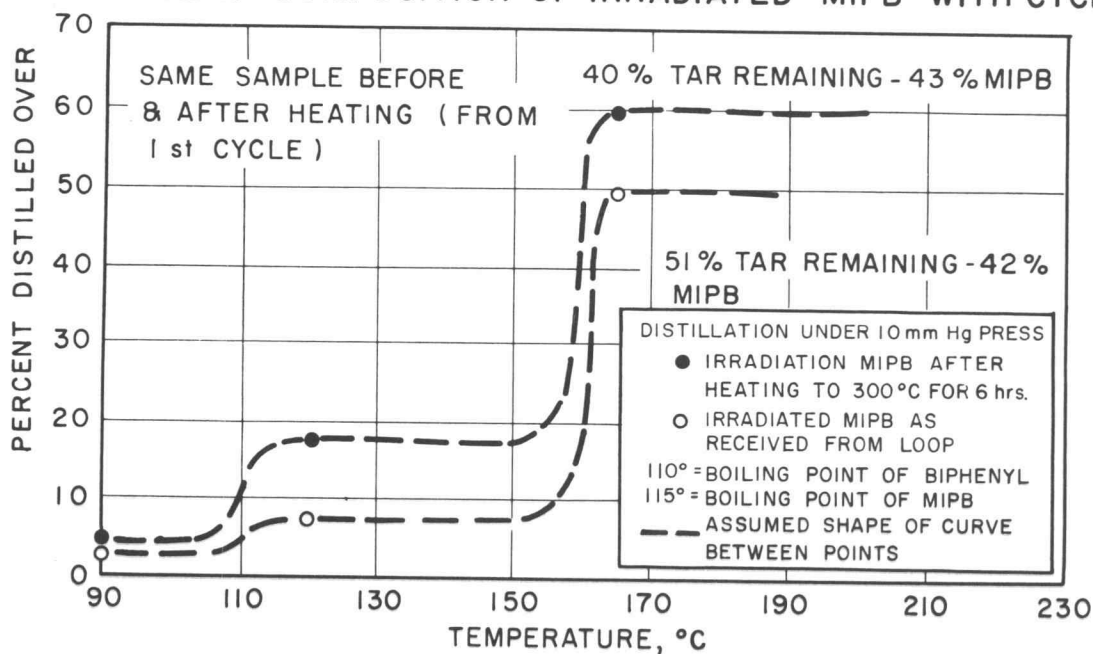
FIGURE 11

CHANGE IN COMPOSITION OF IRRADIATED MIPB WITH HEATING
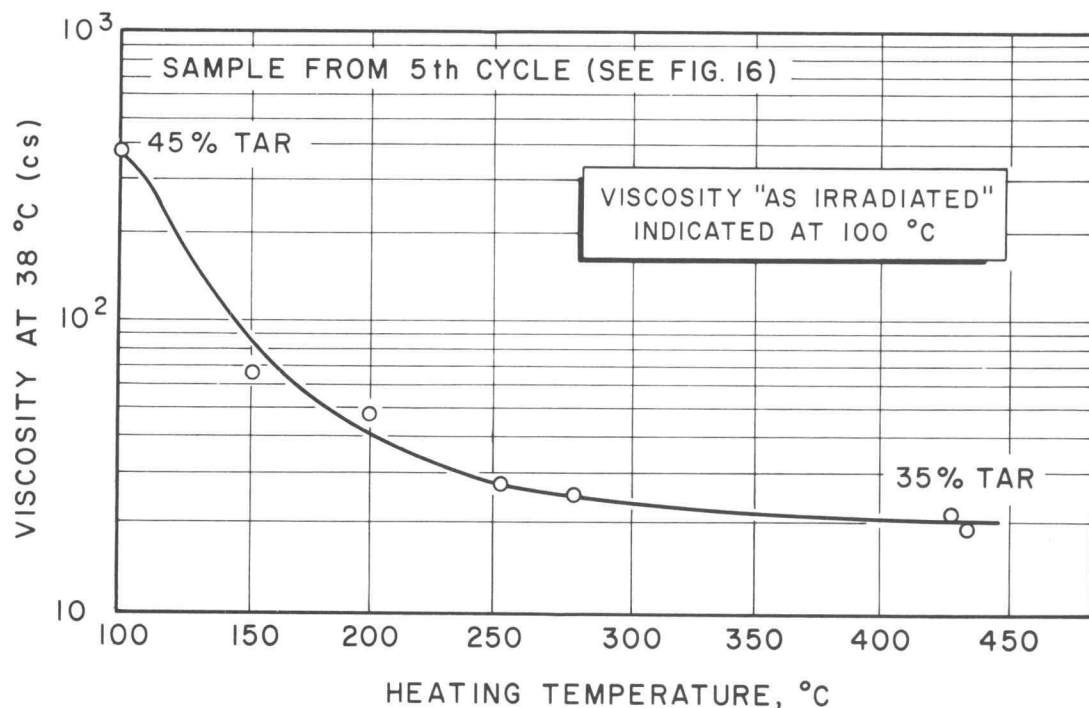
FIGURE 12
IRRADIATED MIPB HEATED FOR SIX HOURS
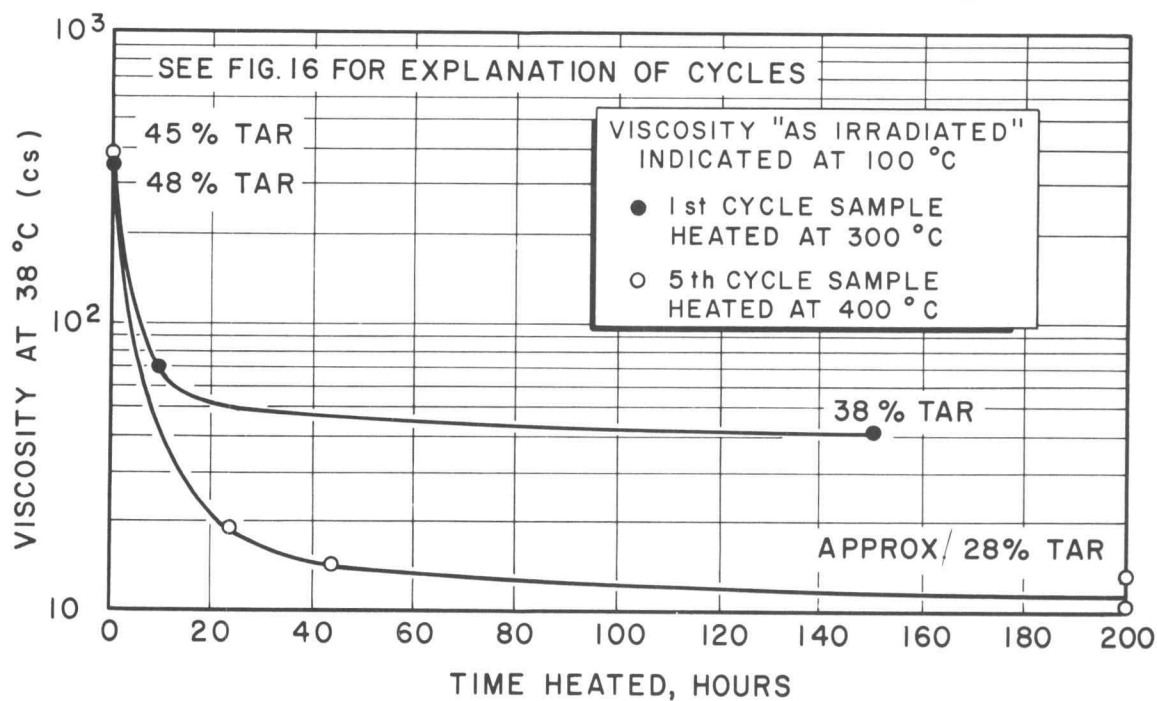
FIGURE 13
IRRADIATED MIPB HEATED AT VARIOUS TEMPERATURES

of the polymer is quite rapid. It is apparent that if the MIPB had been irradiated at a higher temperature, a material of lesser viscosity and less tar content would have been produced.

These observations have considerable importance in determining the laws that govern decomposition as a function of radiation and temperature. This subject is expanded in a later section (entitled Effect of Temperature on Radiolytic Polymerization).

Structure of the Polymers

Because the alkyl group is less stable than the phenyl ring, (3, p. 1) radiation damage to MIPB would be expected to be concentrated mainly in the isopropyl group. The formation of an active site on the alkyl branch should cause a large percentage of polystyrene-type linkages to form. A polymer of the polystyrene type would be expected to be less thermally stable than a polyphenyl-type compound. This may account for the rapid pyrolytic degradation of the MIPB tar.

The eutectic mixture contains no alkyl groups in its original state and should polymerize primarily by phenyl-phenyl linkages. It was found in the pyrolysis studies that an increase in the number of phenyl groups in a nonalkylated polyphenyl causes an increase in the ease of pyrolytic polymerization, (see Part III, section entitled Polymerization Rates). Heating the irradiated eutectic should therefore cause the radiolytic polymers to undergo further polymerization. During the pyrolytic polymerization it is probable that a few single or double phenyl groups are spit off. For example:

$$\phi_4 + \phi_4 \longrightarrow \phi_6 + \phi_2 \quad \text{(a)}$$

(a) The symbol, ϕ_n, as used here is meant to indicate the number, n, of phenyl groups in the polymer.

This process would cause an increase in the average degree of polymerization of the tar, and at the same time cause a decrease in the amount of tar in the coolant. Such an effect was observed. Figure 14 shows that when the irradiated eutectic was heated the amount of tar in solution decreased, but at the same time the viscosity remained about constant or slightly increased. Again using the viscosity-tar content criterion as a measure of polymerization, the polymerization of the tar in the ternary eutectic increased.

As illustrated in Figure 15 this change in tar content is initiated at some temperature below 200 C.

An important point to note is that heating causes a decrease in the amount of radiolytic polymer in the coolant for both alkylated and pure polyphenyls. This occurs in spite of the fact that the mechanisms seem to be different for the alkylated and nonalkylated polyphenyls.

RATE OF RADIOLYTIC POLYMERIZATION

The first step in determining the rate of coolant polymerization is to find the form of the rate law for polymerization. As soon as the rate expression is derived, the decomposition can be defined in terms of the rate constant. The advantage of utilizing a rate law is twofold; first, the rate is associated with a number (the rate constant) that does not change with exposure; and second, the law affords some insight toward the reaction mechanism.

The in-reactor polymerization was found to follow a first order rate law. That is, the rate is directly proportional to the amount of unpolymerized organic in the flux, and is not affected by the presence of tar in solution other than by its inherent action of diluting the pure material.[a] It must be emphasized here that this first order rate law was observed in the case of purely radiolytic damage.

(a) e. g. , A system containing 30 per cent tar contains 70 per cent unpolymerized material, and hence is decomposing at 70 per cent of the rate of the pure material.
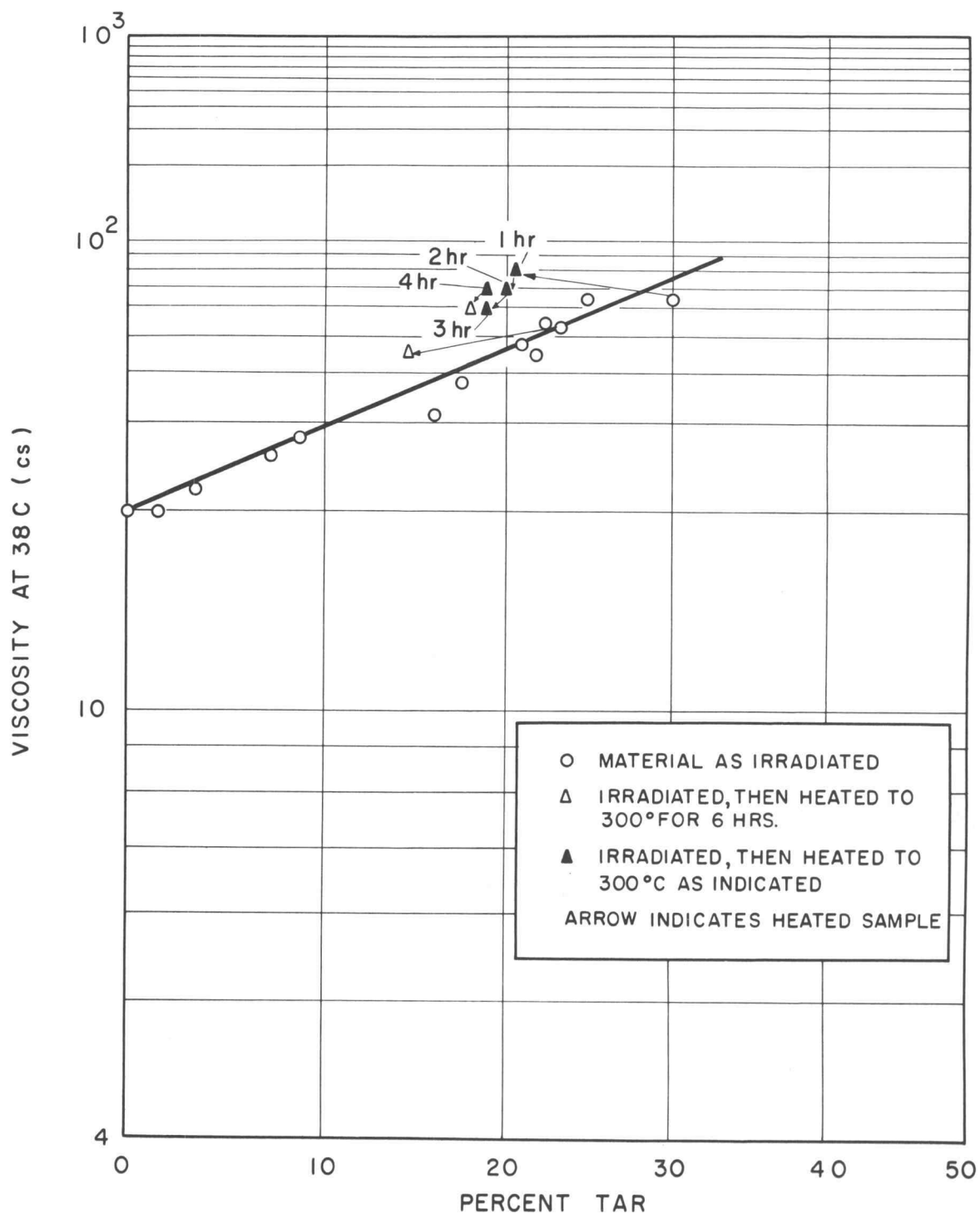
FIGURE 14

VISCOSITY OF IRRADIATED TERNARY EUTECTIC

SAMPLE AS IRRADIATED IS INDICATED
AT 100 °C

ALL DATA ARE FROM THE SAME
SAMPLE OF IRRADIATED EUTECTIC

VISCOSITY AT 38 °C = 64 cs

61 cs

75 cs

PERCENT TAR

HEATING TEMPERATURE (°C)
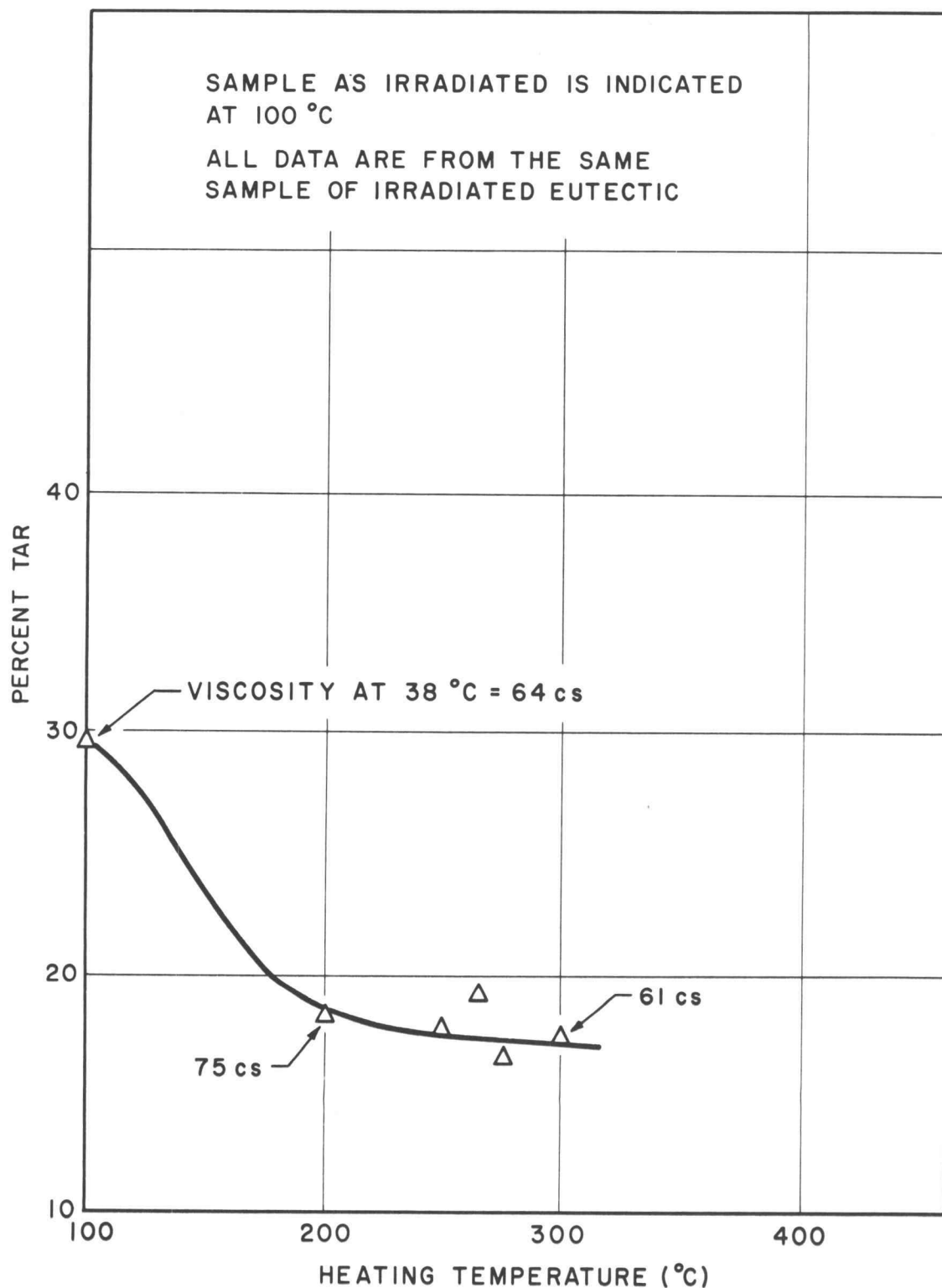
FIGURE 15
IRRADIATED EUTECTIC HEATED FOR SIX HOURS

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In deriving the rate law the fraction of unpolymerized coolant was taken as being that which was not analyzed as tar. A glance at Figure 11 shows that the concentration of low boiling compounds, which according to the above definition would be taken as unpolymerized material, may be from 10 to 30 per cent that of the tar. The only plausible explanation of why the data fit a first order rate law is that most of these lighter fragments polymerize at almost the same rate as the pure material. This is not surprising, because their structures must be similar to the starting material. It is obvious that the entire process during irradiation is very complicated. The chart below lists what appear to be the main radiolytic reactions. The thickness of the arrows roughly indicates the relative importance of the reactions.
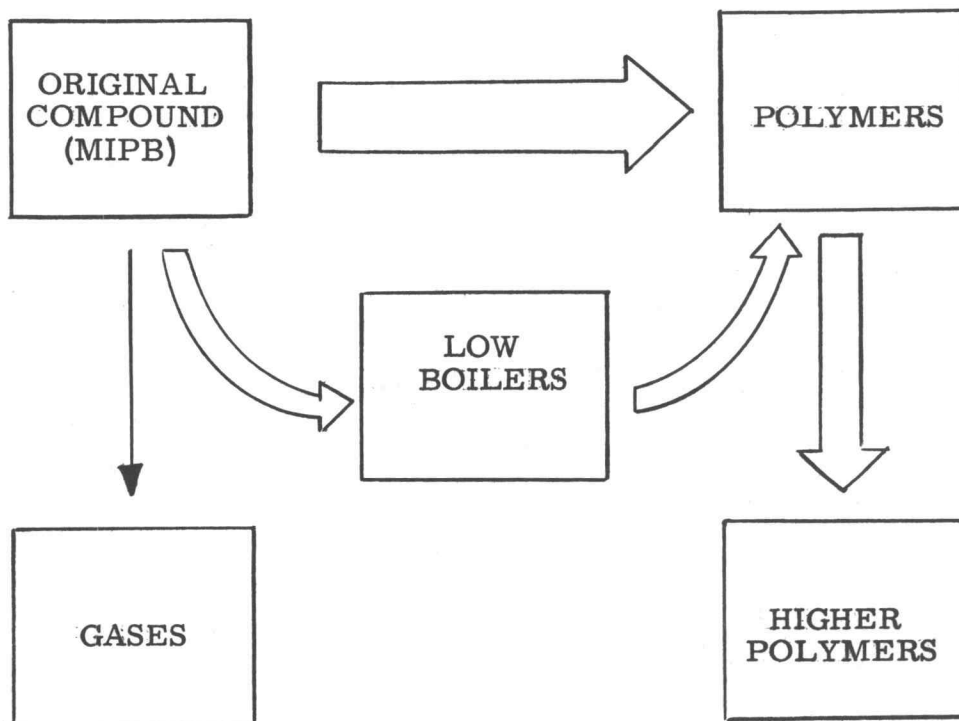
Figures 16 and 17 show the fit of the data to the first order rate law for the MIPB and ternary eutectic runs. The expression against which the data are plotted is the integrated first order rate law expressed in a form applicable to a recirculating system. This expression is:

$$\left(\frac{100 - \text{wt per cent tar}}{100}\right) = e^{-\left[\frac{\text{Wt of coolant in flux}}{\text{Total wt of coolant}}\right](\text{Rate constant})(\text{exposure})}$$

or expressed in symbols:

$$\frac{100 - (\text{per cent tar})}{100} = e^{-(w/W)k\mathcal{E}}$$

This expression is derived below.

First Order Rate Law in a Recirculating System

It is convenient to express the rate law in such a form that the rate constant becomes independent of the geometry of the irradiation facility.

The following notation will be used. Any consistent set of units is suitable.

Symbol	Meaning
C	Fraction of unpolymerized material in organic coolant (1-T)
T	Fraction of tar in organic coolant
W	Total weight of coolant in loop
$\bar{\rho}$	Average density of coolant
v	Volume of coolant in flux zone
w	Weight of coolant in flux zone (ρv)
$\mathcal{E}$	Exposure
k	Rate constant
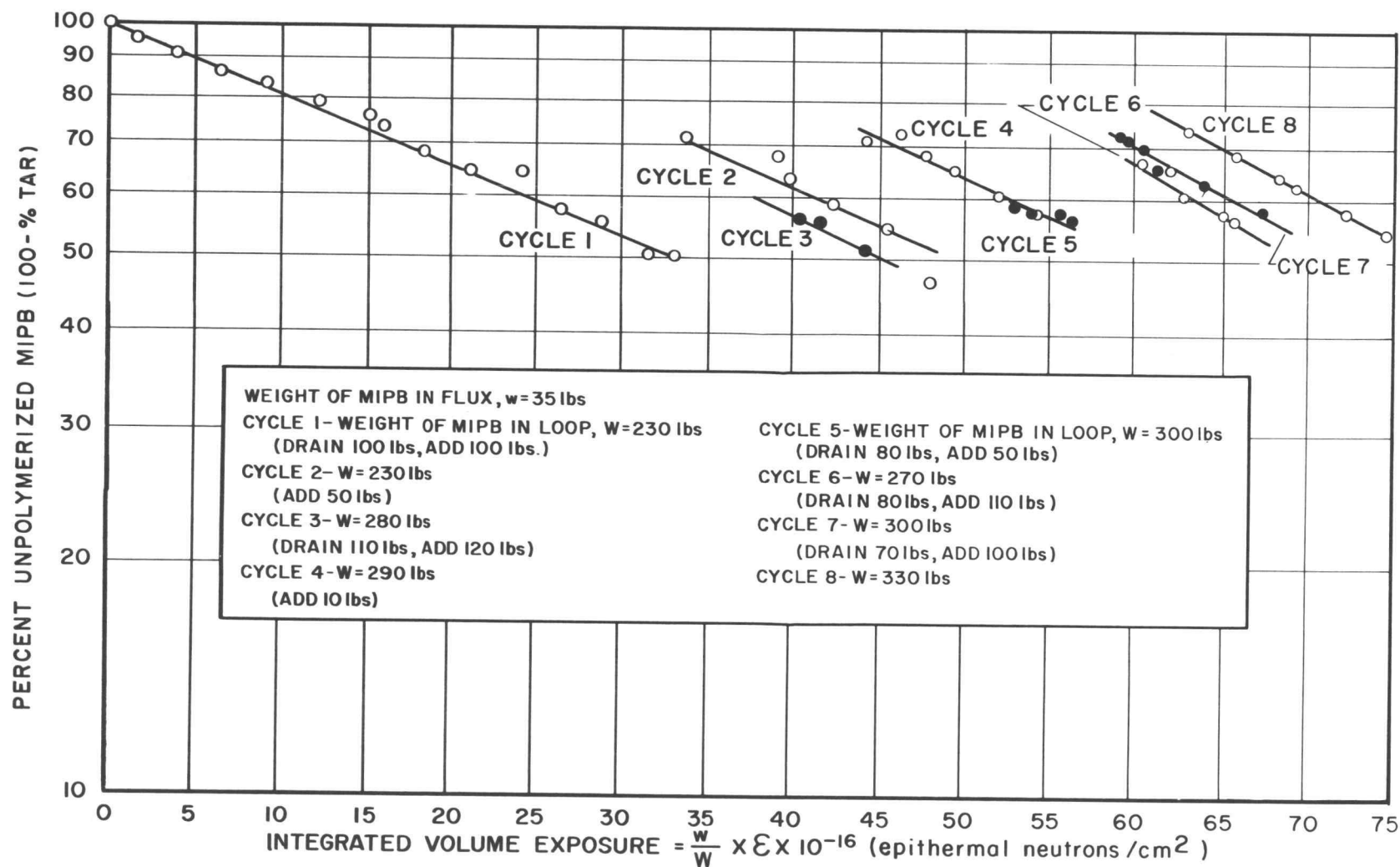
FIGURE 16
POLYMERIZATION OF MIPB
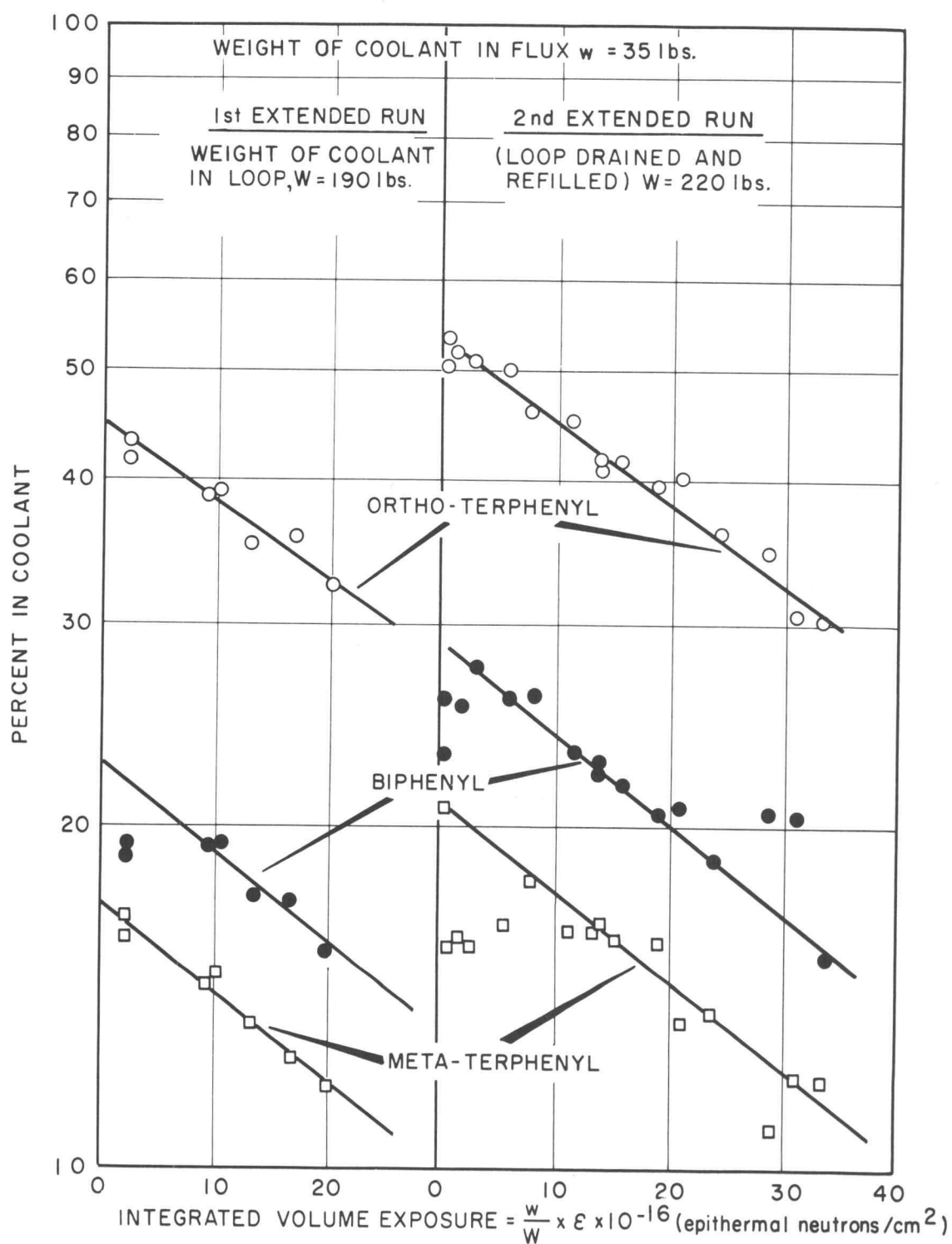
FIGURE 17

POLYMERIZATION OF THE TERNARY EUTECTIC

The first order rate law is:

(Rate of polymerization) = -(Rate Constant) (Amount of unpoly-
merized material in flux)

The amount of unpolymerized material in the flux is $C\rho v$.

The rate of polymerization (with respect to exposure) is:

$$\frac{d\,(\text{Total amount of unpolymerized material})}{d\,\mathcal{E}}$$

The total amount of unpolymerized material in the loop is CW.

The rate law, completely expressed in symbols is:

$$W\frac{dC}{d\mathcal{E}} = -k\,\rho vC$$

If $C = 1$ when $\mathcal{E} = O$ then

$$C = e^{-k\left(\frac{\rho v}{W}\right)\mathcal{E}}$$

Since $C = (1-T)$ the first order law can be expressed as:

$$(1-T) = e^{-k\left(\frac{\rho v}{W}\right)\mathcal{E}} = e^{-k\left(\frac{w}{W}\right)\mathcal{E}}$$

The form of the equation containing the "ρv" term is presented
to bring out the fact that the polymerization rate in a recirculating
system will decrease at high temperature. This effect is independent
of any changes in the polymerization mechanism, and is only a result
of decreasing the number of molecules in the flux because of thermal
expansion.

Stability of the Coolants

The rate constant for a given coolant gives a measure of the
stability of that coolant. The initial polymerization rate is directly
proportional to the rate constant. That is, at low exposures:

$$1-T = e^{-\left(\frac{w}{W}\right)k\mathcal{E}} \cong 1 - \left(\frac{w}{W}\right)k\mathcal{E} \text{ or } T = \frac{w}{W}k\mathcal{E}. \text{ Therefore the}$$

initial rate, $T/\mathcal{E}$, (percent tar formed per neutron) equals $\frac{w}{W}$ k.

The rate constants (the slopes of the lines in Figures 16 and 17) are tabulated below.

TABLE 2
Rate Constants for Radiolytic Polymerization

Compound	Rate Constant $(1\,Mev\;neutrons/cm^2)^{-1\,[a]}$
Ortho-terphenyl	1.7×10^{-18}
Meta-terphenyl	1.7×10^{-18}
Biphenyl	1.8×10^{-18}
MIPB	2.0×10^{-18}

(a) For integrated flux expressed as $\int_o^t \phi_o\, dt$, where ϕ_o is defined in the section on flux measurement, t = seconds.

As was pointed out earlier, the fast component of the flux may vary sufficiently in different locations of the reactor to change the decomposition rate considerably, even if the epithermal flux remains constant. Therefore, although the decomposition rates are expressed accurately as a function of epithermal exposure in the test facility, some caution must be exercised in transposing these data to other reactors or facilities. However, the relative stability measured for the various coolants should be independent of the flux spectrum.

A run with a mixture of MIPB with terphenyls was conducted in order to determine if the MIPB still decomposed in the same manner when it was relatively highly diluted. Figure 18 shows the result of this test. The first order rate law is still followed with the same rate constant. (The lines on the graph are drawn with a slope of 2.0×10^{-18}.) For MIPB the first order law holds over a large range of concentration.
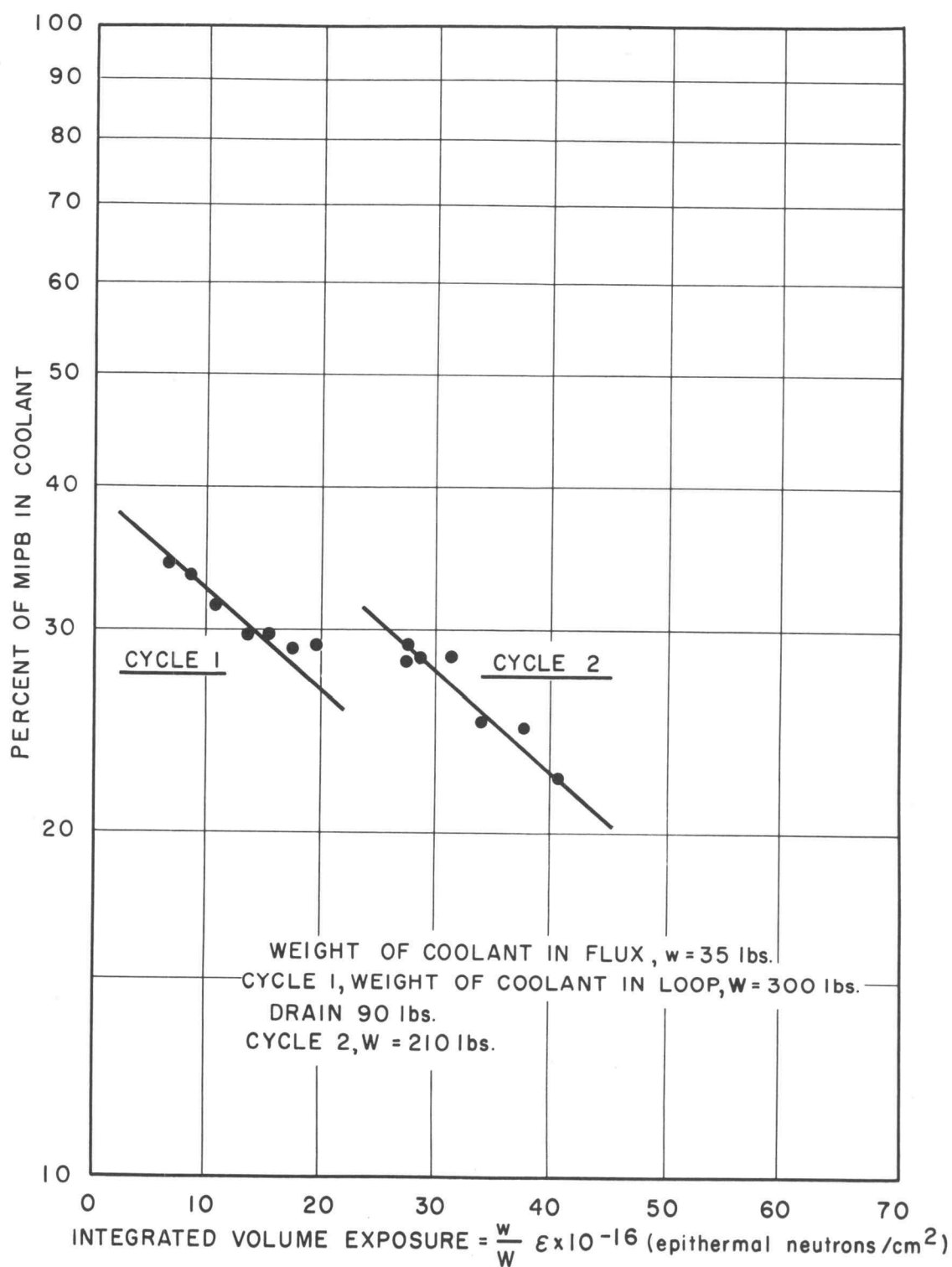
FIGURE 18

POLYMERIZATION OF MIPB MIXED WITH TERPHENYLS

It should be noted that because of the relatively low temperature of the test facility, the rate constants are for radiolytic damage in the absence of pyrolytic damage. The constants for the various materials are seen to be quite similar.

In general, the alkylated polyphenyls have been found to be somewhat less stable than the pure polyphenyls, [a] but this may be a consequence of simultaneous radiolytic and pyrolytic damage. The MIPB is found to be less stable to pyrolytic damage than is biphenyl (See Part III, section entitled Polymerization Rates). In McEwen's experiments, it was found MIPB and biphenyl have the same radiolytic stability; although he found that the eutectic seemed to be more stable (11). The terphenyls usually display a higher radiolytic stability than biphenyl, but some results indicate that only the para-terphenyl is significantly more stable. [b]

According to the experiments in the in-reactor facility, at temperatures below which pyrolytic damage becomes important (around 400 C), the MIPB has about the same stability as the ternary eutectic mixture.

It is interesting to compare the MIPB decomposition data obtained in this facility with that obtained at Brookhaven by Monsanto and Mine Safety Appliances Company (11), (12). If their data are used to calculate a rate constant on the same basis that was used above, then $k = 0.6 \times 10^{-18}$ (epithermal neutrons/$cm^2)^{-1}$. The over-all decomposition rate at BNL was therefore about one third of that observed in the above experiments when compared on the basis of

---

(a) This conclusion is based mostly on measurements of stability derived from viscosity changes and gas evolution. Much of this work was done by the California Research Corporation for irradiations at high temperatures, and is presented in their periodic reports (2).

(b) Again these conclusions are based primarily on gas evolution studies (13, p. 6-17), (14, p. 6-13).

epithermal neutron dosage. Part of this discrepancy may be due to differences in the fast flux spectra or to differences in the ratios of gamma to neutron dose rates. It is also likely that the Brookhaven fluxes were not as high as reported, since the flux in the Brookhaven test hole was monitored before inserting the stainless steel test facility. Even if the above mentioned factors could be corrected for, it is likely that the BNL rates would still be somewhat lower than rates obtained here. As will be shown immediately below, an effect in this direction is expected because the BNL loop ran hotter (about 260 C) than did our loop.

EFFECT OF TEMPERATURE ON RADIOLYTIC POLYMERIZATION

When the above experiments are considered it becomes apparent that if a polyphenyl coolant is irradiated at an elevated temperature part of the tar formed by radiolysis will be destroyed by pyrolytic degradation. In this situation the rate law for polymerization should be of the following form:

$$\frac{dC}{dt} = -\left[k_1 C - k_2 T\right] = -\left[(k_1 + k_2) C - k_2\right]$$

The derivation of this law is based on five assumptions.

(1) The radiolytic polymerization is proportional to the amount of unpolymerized compound. (This has been proved)

(2) The pyrolytic polymerization is proportional to the amount of unpolymerized compound. (This has been proved)

(3) The radiolytic degradation of the polymer is proportional to the amount of polymer present (This has not been proved)

(4) The pyrolytic degradation of the polymer is proportional to the amount of polymer present. (This has not been proved)

(5) The net effect of the four above reactions is the same as the sum of their individual effects. (This will be partially proved in the section on Combined Radiolytic and Pyrolytic Decomposition.)

The following symbology will be used:

Symbol	Meaning
C	Fraction of unpolymerized coolant (1-T)
T	Fraction of tar
$\mathcal{E}$	Exposure
k_R	Rate constant; Radiolytic polymerization
k_T	Rate constant; Pyrolytic polymerization
k_{RP}	Rate constant; Radiolytic degradation of polymer
k_{TP}	Rate constant; Pyrolytic degradation of polymer
w	Weight of coolant in flux zone
W	Total weight of coolant in loop
ϕ	Flux (Note: $\mathcal{E}/\phi$ = time)

k_1 and k_2 will be defined during the derivation.

The pyrolytic rate constants are temperature dependent so that the rate law derived below is for a particular temperature.

The radiolytic polymerization rate depends on the amount of organic in the flux. The pyrolytic polymerization depends on the total amount of organic in the loop system. (Only the isothermal case is considered.)

The rate law is therefore:

$$W\frac{dC}{d\mathcal{E}} = -\left[k_R wC + \frac{k_T WC}{\phi} - k_{RP}wT - \frac{k_{TP}}{\phi}WT \right]$$

The flux, ϕ, was introduced into this equation to convert the units for the pyrolysis rate constants from time to exposure so that the entire equation is in consistant units. To simplify the writing, the terms will be immediately lumped together:

$$k_1 = k_R\frac{w}{W} + k_T/\phi \text{ (the combined constant for polymerization)}$$

$$k_2 = k_{RP} + k_{TP}/\phi \text{ (the combined constant for degradation of the polymer)}$$

Both k_1 and k_2 are now in terms of (inverse) exposure.

Using these terms, and remembering that $T = 1-C$

$$\frac{dC}{d\mathcal{E}} = -\left[k_1 C - k_2 T\right] = -\left[(k_1 + k_2)C - k_2\right]$$

The integrated form is

$$\frac{1}{k_1 + k_2} \ln\left[\frac{C(k_1 + k_2) - k_2}{k_1}\right] = -\mathcal{E}$$

k_1 can be evaluated by taking the initial rate extrapolated back to $\mathcal{E} = 0$. At this point $T = 0$, $C = 1$, and $\frac{dC}{d\mathcal{E}} = -k_1$. k_2 can then be evaluated by using the data at some high exposure point.

For capsule irradiations $\frac{w}{W} = 1$.

Figure 19 shows the fit of this modified rate law to data obtained by Colichman and Fish on the irradiation of meta-terphenyl by electrons at high temperature (6). It is seen that the fit of the modified rate law to these data is good. The first order rate law is obviously not valid for this case. The higher initial rate at 450 C is expected because of the greater rate of pyrolytic polymerization at the higher temperature. This is a separate effect from the pyrolytic degradation of the polymer.

Figure 20 shows the decomposition of para-terphenyl as measured by the same authors. At 400 C there seems to be essentially no reverse reaction since a first order rate law is followed. This indicates a greater temperature stability of the para-terphenyl polymers.
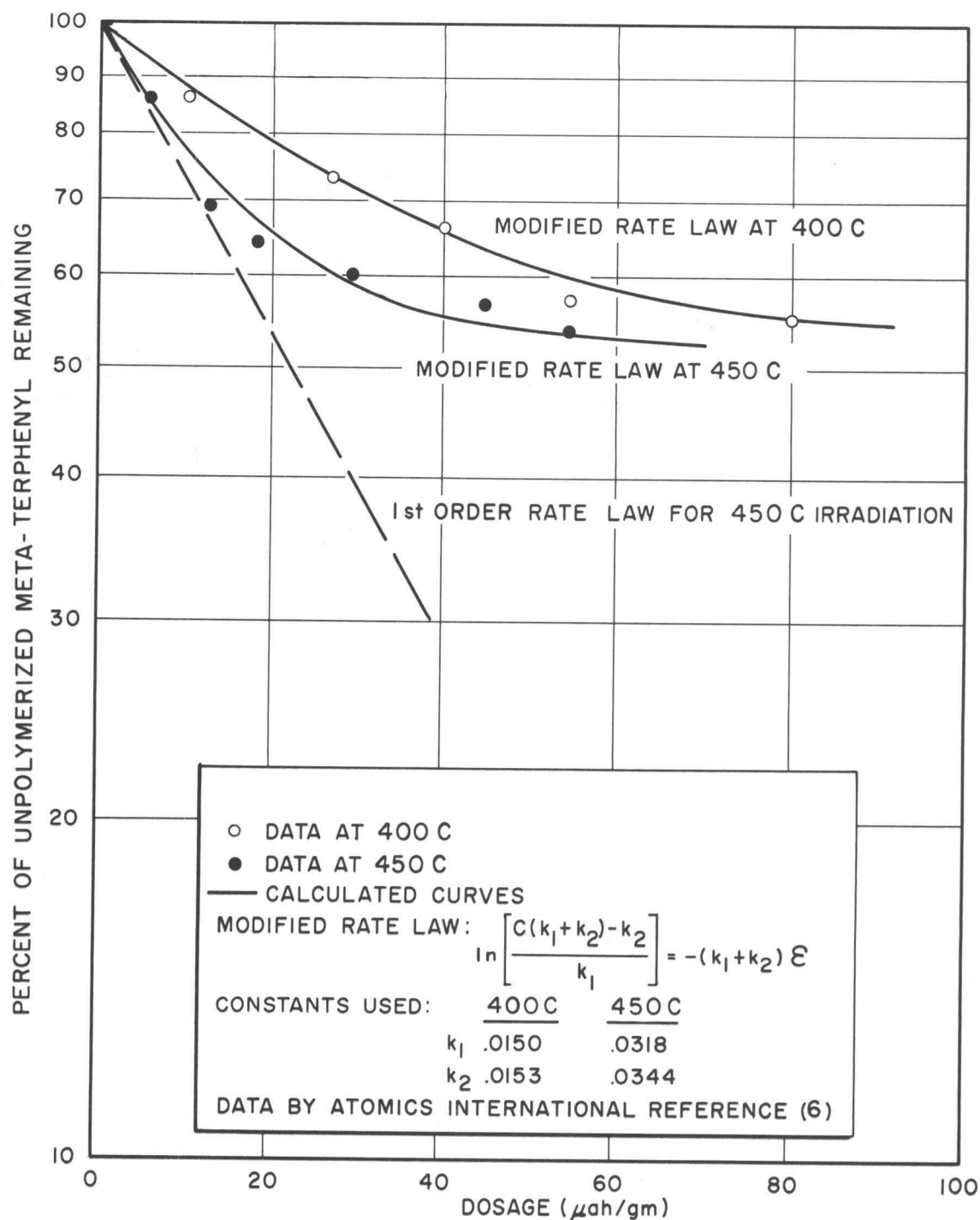
FIGURE 19

POLYMERIZATION OF META-TERPHENYL BY ONE MEV ELECTRONS
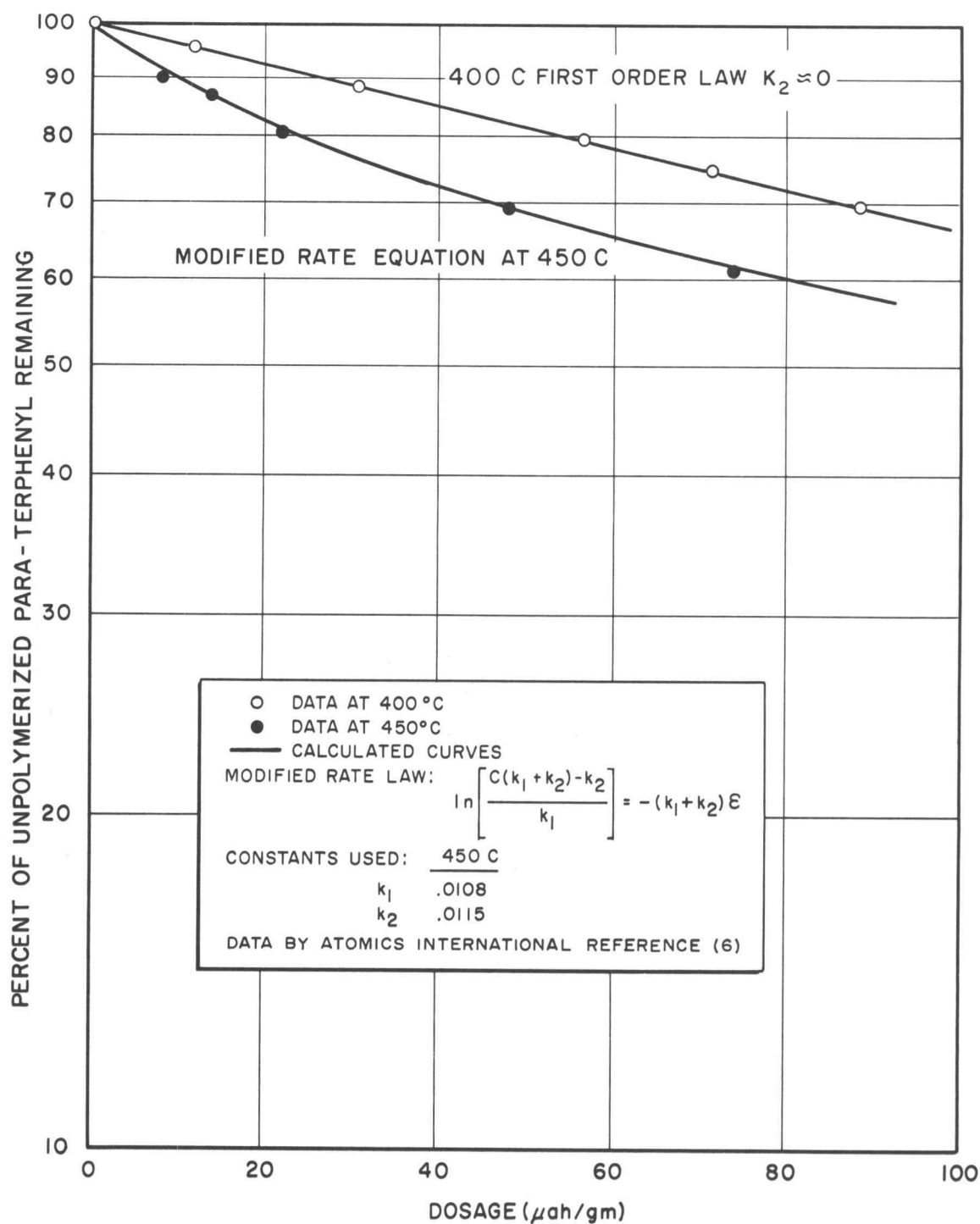
FIGURE 20

POLYMERIZATION OF PARA-TERPHENYL BY ONE MEV ELECTRONS

PART II - RADIOLYTIC DECOMPOSITION BY GAMMA RAYS

EXPERIMENTAL PROCEDURE

The only compound that was exposed to gamma radiation was MIPB. About 10 ml of the MIPB to be irradiated was placed in a test tube without attempting to remove any dissolved air from the liquid. The test tubes were then stoppered with a cork that had been notched for the purpose of relieving pressure build-up caused by decomposition gases. The MIPB, therefore, had limited access to air throughout the irradiation.

One set of MIPB samples, that were to be irradiated, were first exposed for several months to air until the liquid turned a light yellow because of partial oxidation. These samples were found to contain about 0.2 per cent of high boiling compounds that were detected by the normal tar analysis. The purpose of this experiment was to determine if the presence of a small amount of oxidation products might in some way change the polymerization rates.

The MIPB samples were placed near a Co^{60} source in a position where the dose rate was 1.4×10^6 Roentgens per hour. During the irradiation the temperature of the samples was from 15 to 25 C.

DECOMPOSITION OF MIPB

Decomposition Products

As in the experiments on reactor irradiation of organic cool-ants; the examination of the decomposition products is based primarily on a tar-viscosity plot. Figure 21 is such a plot for the gamma irradiated MIPB samples. It is seen that the slight pre-oxidation of some of the samples had no effect on their viscosity.

It is also noted that there is no significant difference between the viscosity of the gamma irradiated samples and the reactor irradiated samples. In the concluding section on gamma ray damage it is

FIGURE 21

VISCOSITY OF GAMMA IRRADIATED MIPB

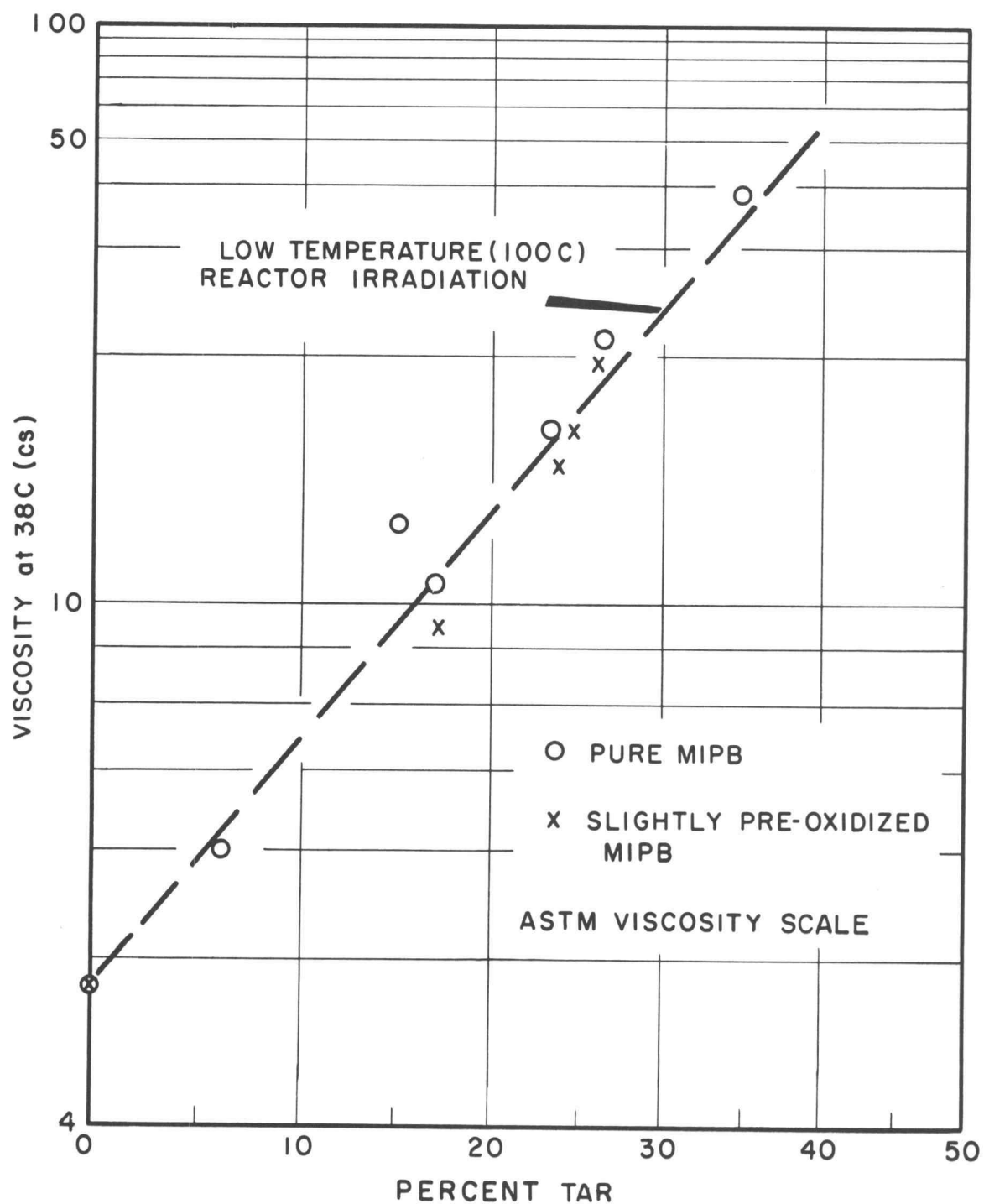shown that about 75 per cent of the in-reactor damage was caused by fast neutrons with the remainder caused mainly by gamma rays. Because of the similarity between the tar-viscosity plots for reactor irradiated (i.e., mainly neutron irradiated) and purely gamma irradiated MIPB, it can be concluded that the polymers formed by fast neutron or gamma radiolysis have similar structures.

The products formed by gamma and neutron irradiation were also compared by infra-red absorption measurements. With one exception, that may be an indication of a basic difference in the mechanism of gamma ray and neutron radiolysis, the absorption spectra were very similar. At 12.60 microns a strong absorption band occurred in the gamma irradiated samples that was not evident in the reactor irradiated samples. However, if the reactor irradiated MIPB (which was irradiated at about 100 C) was distilled at 195 C, this absorption band appeared strongly in the distillate. These spectra are illustrated in Figure 22. Thus, the compound responsible for the 12.60 micron absorption must be one of the lighter products, not included in the tar, and apparently is formed by heating irradiated MIPB.[a]

These observations may indicate that as the gamma energy is absorbed by the MIPB molecule, it spreads out causing a general "heating" of the molecule. In this manner the MIPB would be effectively heated and irradiated at the same time by gamma rays, thereby producing the infra-red absorbent product. Most of the fast neutrons, because of their higher energies, may knock off a part of the molecule before the collision energy can spread out through the molecule. Considerable liberty was taken in the interpretation of these data, however, Bolt and Carrol have previously hypothized differences of a similar type (3, p. 6).

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[a] This band does not appear in MIPB decomposed by pyrolytic action in the absence of irradiation.
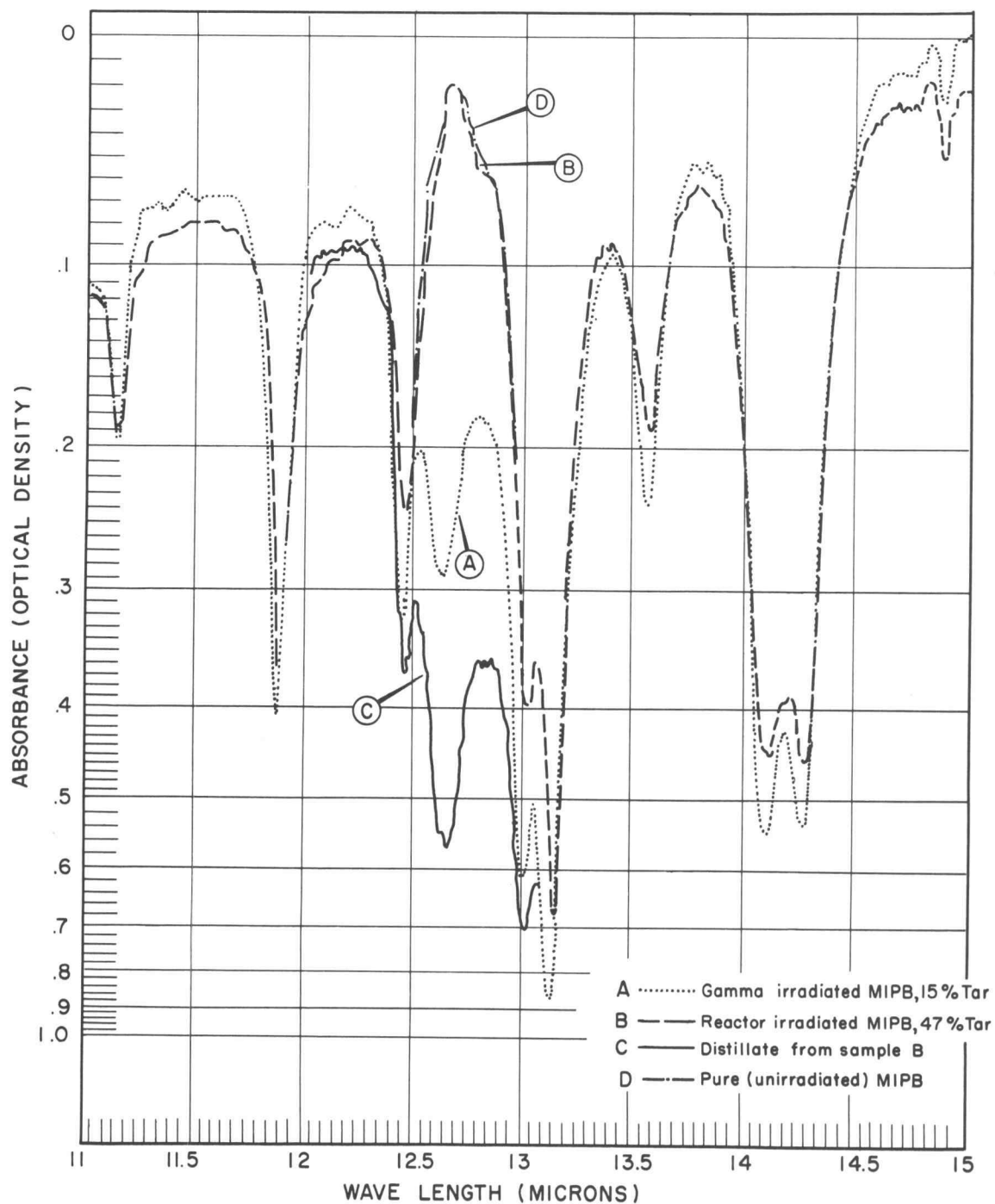
FIGURE 22

INFRA-RED SPECTRA OF IRRADIATED MIPB
($30 \, mg/ml$ in CS_2)

A .... Gamma irradiated MIPB, 15% Tar
B — — — Reactor irradiated MIPB, 47% Tar
C ————— Distillate from sample B
D —·—·— Pure (unirradiated) MIPB

Polymerization Rates

Under the influence of gamma radiation the MIPB was again found to polymerize according to a first order rate law. Figure 23 is a plot of the logarithm of the amount of unpolymerized MIPB as a function of gamma dosage. The fit to a straight line, indicating a first order rate law, is apparent.

The rate constant, k, is 6.2×10^{-11} Roentgens^{-1} with the rate equation written as:

$$\frac{dC}{dR} = -kC$$

C is the fraction of unpolymerized MIPB and R is the exposure in Roentgens.

In the case of the samples that were pre-oxidized, there is an accelerated initial rate, after which the rate is the same as for the un-oxidized MIPB samples. Apparently the presence of some oxidation products in the MIPB has little effect on decomposition rates.

The measured rate may include some effect due to an increased rate of oxidation of the MIPB by the air in the containers during irradiation. However, in some experiments by Shell Development Company designed to investigate the effect of radiation on the oxidation of polyphenyl ethers, very little increased oxidation was observed (15, p.5-6).

COMPARATIVE DESTRUCTION BY GAMMA RAYS AND NEUTRONS

The fraction of the decomposition that is caused by gamma rays in any given test facility is, of course, dependent on the relative neutron to gamma flux in that facility. The rate of gamma damage during the in-reactor experiments can be calculated from the rate constant for gamma polymerization and the ratio of gamma dose to neutron exposure in the in-reactor facility. During an integrated epithermal neutron exposure of 10^{18} neutrons/cm^2 the gamma dose
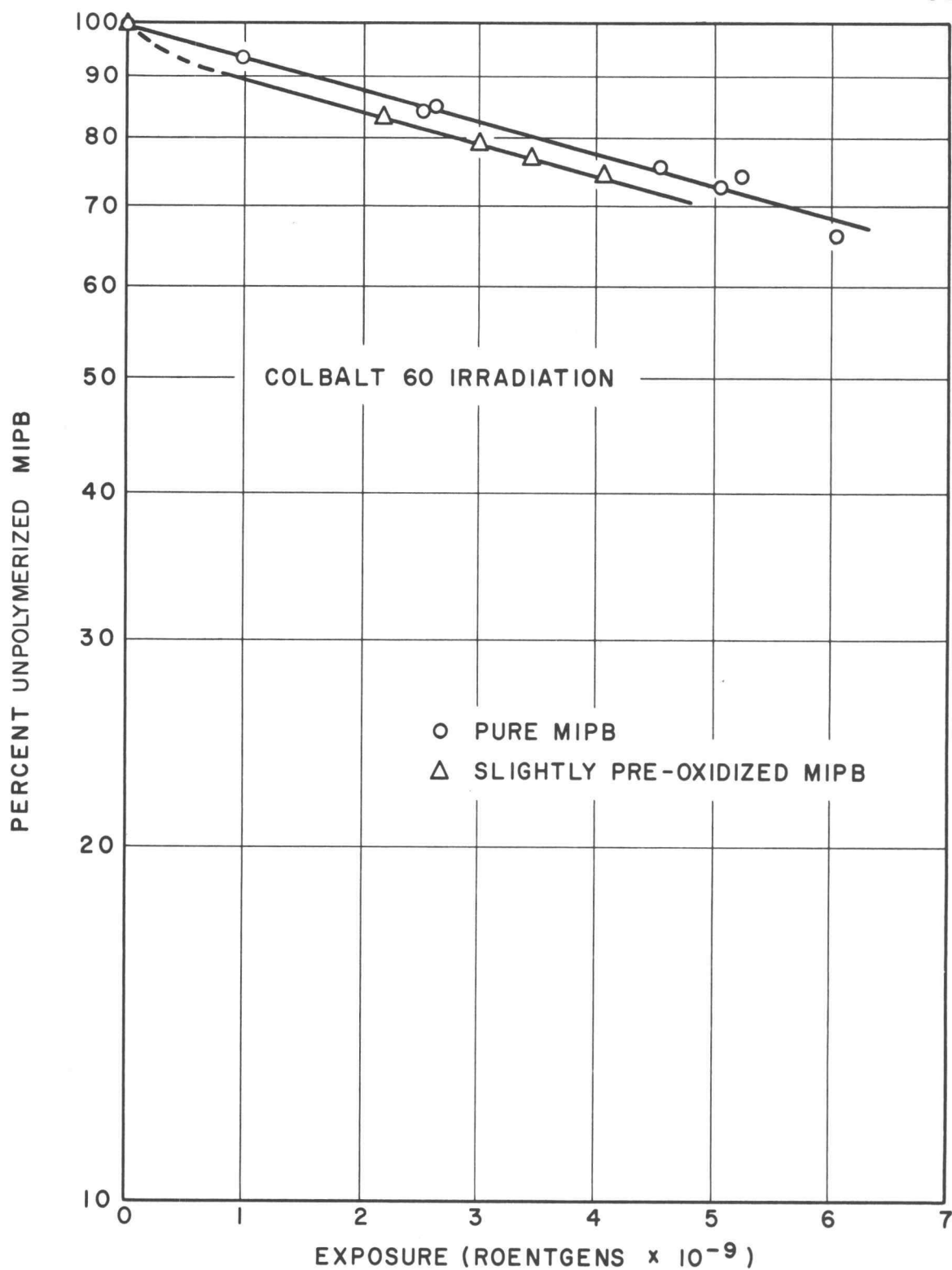
FIGURE 23
POLYMERIZATION OF MIPB BY GAMMA RAYS

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was measured to be 8×10^9 Roentgens. This means that rate constant for polymerization by gamma rays in the in-reactor test facility is:

$$(6.2 \times 10^{-11}) \ (\frac{8 \times 10^9}{10^{18}}) = 0.5 \times 10^{-18}$$

per epithermal neutron/cm^2. Since the rate constant for total radiolytic damage to MIPB is 2.0×10^{-18} per epithermal neutron/cm^2, the gamma rays caused 25 per cent of the radiolytic polymerization in the reactor irradiation experiments.

In addition to the comparison of over-all damage rates, it is interesting to compare the ratio of gamma to neutron damage on an equal energy absorption basis. There has been some theoretical reasoning and experimental evidence which indicates that the damage caused by any type of radiation should only be dependent on the energy absorbed by the organic from the radiation (3), (5), (7), (17). In other words, the damage caused by the absorption of 1 mev of gamma energy should be the same as that caused by the absorption of 1 mev of neutron energy. It has also been recognized that the range over which the energy is delivered can be important (3, p. 6), (22). The short range particles, such as alpha particles, concentrate the energy over a small volume, and may have a larger detrimental effect on an individual molecule. The same reasoning can also apply, to some extent, between the action of highly energetic neutrons (several mev), and gamma rays (1 to 2 mev). Most of the experimental evidence has been reviewed by Colichman (5), and he concludes that there is approximately equivalent radiation damage in organic materials for equivalent energy deposition. The word "approximately" is emphasized since many of the experimental comparisons show a scatter of a factor of 1.5 or greater.

There are no measurements of the fast neutron spectrum taken in the in-reactor test facility, so that the energy absorbed from neutrons cannot be accurately stated. However, there are enough data available from the experiments to allow an estimate to be made of the relative damaging power of neutrons and gamma rays.

An integration of the rate law for gamma decomposition gives:

$$\frac{N}{N_o} = e^{-(6.2 \times 10^{-11})R}$$

where: R is the exposure in Roentgens

N is the number of unpolymerized MIPB molecules/cm^3

N_o is the original number of MIPB molecules/cm^3 (When R = O)

$\Delta N = N_o - N$ = number of molecules polymerized/cm^3

$$\frac{N}{N_o} \simeq 1 - 6.2 \times 10^{-11} \text{ after 1 R exposure}$$

$$\Delta N = 6.2 \times 10^{-11} N_o \text{ per R (for small R)}$$

A calculation based on electron density gives an energy absorption of 5.7×10^{13} ev per gram of MIPB per Roentgen.[a] This is equivalent to 5.8×10^{13} ev per cm^3 of MIPB per Roentgen.

$$G = \frac{\text{molecules polymerized}}{100 \text{ ev absorbed}} = \frac{6.2 \times 10^{-11} N_o}{(5.8 \times 10^{13})(10^{-2})}$$

$$= 1.1 \times 10^{-22} N_o \text{ [b]}$$

$$N_o = 3.0 \times 10^{21} \text{ molecules/}cm^3 \text{ for MIPB}$$

$$\therefore G = 0.33 \text{ for polymer formation by gamma rays in MIPB}$$

(a) Compared with 5.3×10^{13} ev/gram of air per Roentgen.

(b) G is normally defined as molecules formed per 100 ev absorbed. The G defined here is more useful for the present work.

The problem of calculating the energy absorbed from neutrons is somewhat more complex. The available neutron energy passing through the organic per second is $\int_0^\infty \phi(E) E \, dE$ where $\phi(E)$ is the flux of energy, E.

The amount of energy absorbed per second per cm^3 of the MIPB is given by:

$$\int_0^\infty \phi(E) E \, 10^{-24} \psi(E) \, \eta \, dE$$

$\psi(E)$ is an energy dependent function (defined in Part I, section entitled Neutron Damage) that contains the scattering cross sections and the average amount of energy transferred per collision with a C-H pair. It expresses the fraction of available energy that is absorbed. (The 10^{-24} factor arises because $\psi(E)$ is expressed in barns.)

η is the number of C-H pairs per cm^3 of MIPB. $\eta \simeq 15.5 \, N_o$.

The values of

$$D = \int_0^\infty \phi(E) E \, \psi(E) \, dE$$

have been calculated (See Part I, section entitled Neutron Damage) for a flux spectrum near the fuel and for a moderated spectrum. It is suspected that the spectrum in our reactor facility resembles the moderated spectrum, but actually is somewhat more energetic. No high energy neutron measurements have been made in the test facility.

Based on a flux spectrum normalized such that the flux at an energy of 1 mev is 1 neutron/cm^2, sec, the following D values were calculated:

Near Fuel, D = 20

Moderated, D = 8.3

Under the "moderated" condition the total energy absorbed in 1 cm^3 of MIPB per second is:

$$(8.3)(10^{-24})(15.5\ N_O) = 1.3 \times 10^{-22}\ N_O\ \text{mev/cm}^3,\ \text{sec}$$

The rate constant for polymerization of MIPB by reactor neutrons was calculated to be 1.5×10^{-18} per epithermal neutron/cm^2 (after being corrected for the in-reactor gamma radiation).

At unit flux:

$$\Delta N = 1.5 \times 10^{-18}\ N_O\ \text{molecules polymerized cm}^3\ \text{per second}$$
(for small exposures)

$$G = \frac{\text{molecules polymerized}}{100\ \text{ev absorbed}} = \frac{1.5 \times 10^{-18}\ N_O}{(1.3 \times 10^{-22} N_O)(10^6)(10^{-2})}$$

$$= 1.2\ \text{for polymer formation by neutrons in MIPB}$$
(moderated flux)

In a similar manner,

$$G = 0.47\ \text{in the "near fuel" position.}$$

The G for gamma ray polymerization was almost the same (0.33) as the neutron damage G factor in the "near fuel" position. However, the test facility neutron spectrum most likely had less of a high energy component than the "near fuel" spectrum. Based on the most probable shape of the neutron spectrum in the test facility, [a] it is concluded that for equal energy absorption fast neutrons are some- what (most likely 50 to 200 per cent) more damaging than gamma rays.

(a) Guessed to be somewhere between the two spectra chosen as illustrations.

PART III - PYROLYTIC DECOMPOSITION

TEST MATERIALS

Ortho-, meta-, and para-terphenyl, biphenyl, MIPB, and mono-methylbiphenyl (MMB) were studied in the experiments on pyrolytic decomposition. All of these materials, with the exception of the MMB, were from the same sources and of same purity as those used in the radiolytic decomposition experiments.

The MMB was investigated because some experiments at the California Research Corporation showed that this compound is more stable than polyphenyls with longer alkyl groups.[a] The Dow Chemical Company produced the MMB used in these experiments in a small (4 lb) pilot batch. The material, as received, analyzed as 85 to 87 per cent MMB, nine per cent dimethylbiphenyl, and the remainder primarily as higher methyl-biphenyls. The MMB is a mixture of mostly the meta and para isomers in an undetermined ratio.

The MMB was redistilled at a pressure of 30 mm of mercury and the fraction, about half of the sample, that distilled over before the temperature started to rise was separated and utilized in the experiments. Based on a comparison with infra-red spectra curves received from the California Research Corporation, the distillate contained very little of the poly-methylbiphenyls.

The pour point of MMB is -35 C and the normal boiling point is about 270 C. This material is slightly less viscous than MIPB.

EXPERIMENTAL PROCEDURE

About 35 ml of the material to be investigated were loaded into a glass liner and placed in a manganese steel reaction vessel. The purpose of the glass liner was to prevent the organic material from

[a] Private communication with James G. Carrol of the California Research Corporation

coming into contact with the steel walls of the vessel during pyrolysis. Tilicheev reports that certain materials of construction of the reaction vessel will effect the rate of pyrolysis of benzene (18). In particular he noticed a slight catalyzing effect of nickel. In a few of the pyrolysis experiments reported below a fraction of the sample had leaked from the glass liner and had contacted the steel wall of the vessel during the experiment. In these cases the portion of the sample from the glass liner and from the unlined reaction vessel were analyzed separately. No difference was ever found in the rate of polymerization of the two samples, so that the precaution of utilizing a glass liner was apparently not necessary for these experiments.

After the glass liner had been filled and placed in the reaction vessel, the vessel was attached to a vacuum pump for about 1/2 hour in order to remove any dissolved air. For the first few minutes the samples would normally effervesce, indicating that the air was being removed. If the compound was a solid this step was omitted. After deaerification the vessel was flushed and filled with helium and then sealed. The reaction vessels were placed in an oven and heated for the prescribed time.

The temperature of the oven was indicated by chromel-alumel thermocouple that had previously been calibrated against a National Bureau of Standards thermocouple. During the runs the oven controller maintained the temperature so that it fluctuated no more than 2.5 C around the set point. Some of the early decomposition data were taken before the installation of the calibrated thermocouple. The temperature measured during these tests was some unknown amount lower than the true temperature. Only the data taken with the calibrated thermocouple are used for the decomposition rate calculations, although the earlier data are utilized in the study of the decomposition products.

DECOMPOSITION OF THE COOLANTS

MIPB Decomposition Products

Only the decomposition products of pyrolytically decomposed MIPB were studied, since only with MIPB were there any radiolytic decomposition data available for comparison purposes. Again, the primary evaluation was made on the basis of a viscosity-tar plot. These data are presented in Figure 24. It is readily noted that the viscosity of the pyrolytically decomposed MIPB is less than that of the radiolytically decomposed MIPB. This indicates a lesser degree of polymerization for the pyrolytically produced tars. Within the range over which these experiments were conducted there is no significant effect of the test temperature on the viscosity or, hence, polymer structure.

The examination of the pyrolytically decomposed MIPB by infra-red methods showed that certain absorption bands in the MIPB weakened to a greater extent than could be explained by transformation to tar. (For example, there is a strong absorption band in MIPB at 3.40 microns. In one pyrolytically decomposed sample that was analyzed as containing 15 per cent tar, the absorption at 3.40 microns was 30 per cent less than for pure MIPB.) The unaccounted for weakening of the absorption bands can be explained by the destruction of MIPB with the formation of low boiling compounds that are not detected as tar.

Low boiling compounds are also formed by radiolytic action, but to a lesser extent than by pyrolytic action. In the case of radiolytic damage the infra-red absorption bands generally decrease to a lesser extent than would be predicted from the tar content. This indicates that the molecular features that cause the infra-red absorption in MIPB are also present to some extent in the radiolytic polymers.
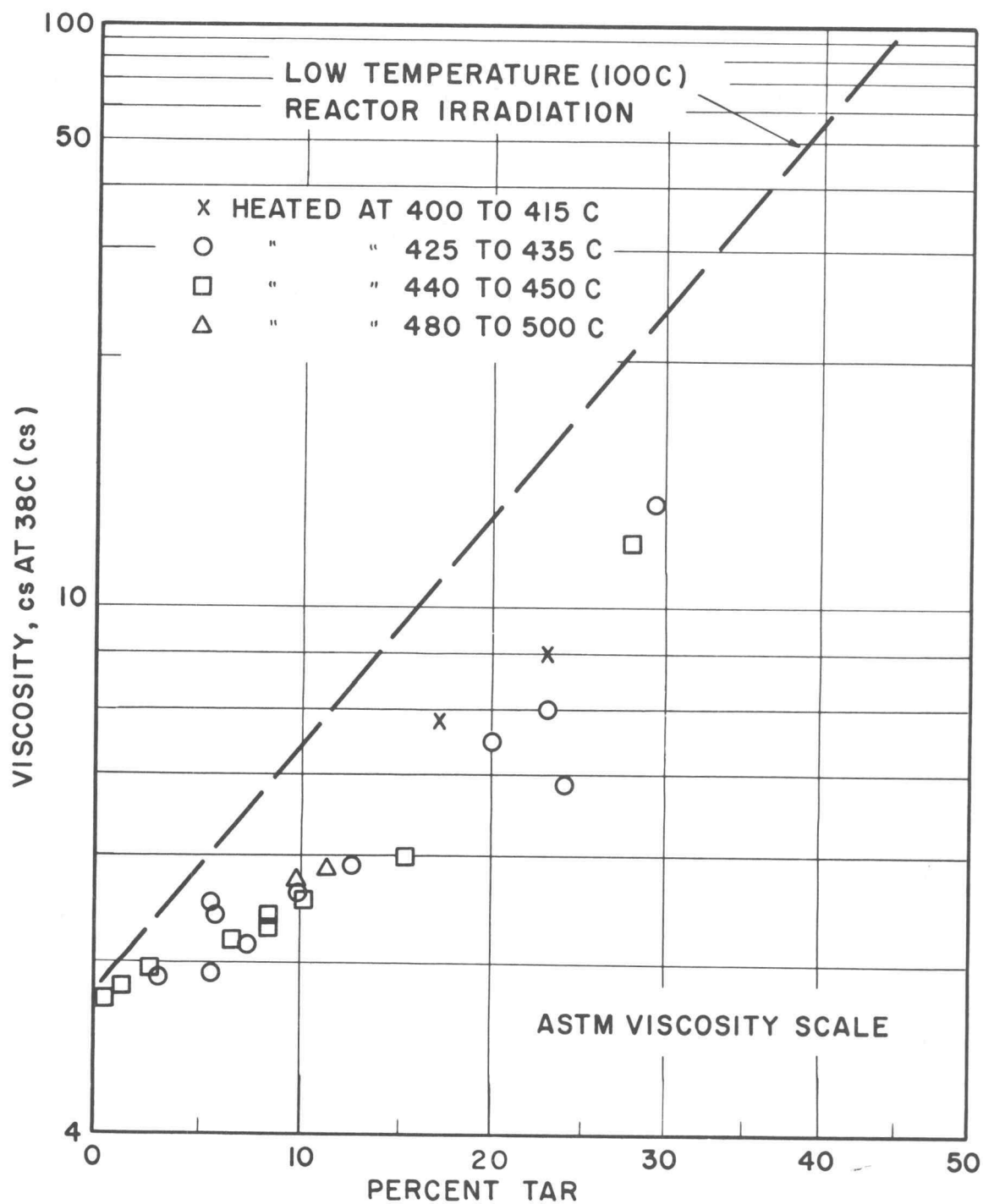
FIGURE 24

VISCOSITY OF PYROLYTICALLY DECOMPOSED MIPB

Polymerization Rates

The rates for pyrolytic damage are computed on the basis of polymer formation in the same manner as were those for radiolytic damage.

Again the polymerization follows a first order rate law:

$$\frac{dC}{dt} = -kC$$

C is the fraction of unpolymerized coolant, t is the time in hours, and k is the rate constant. In Figures 25 and 26 the pyrolytic polymerization of MIPB and ortho-terphenyl is shown to follow the first order law.

The rate constants have been measured at several temperatures, and have been found to vary with temperature according to the Arrhenius relationship:

$$k = Ae^{-E_a/RT}$$

k is again the rate constant, A is a proportionality constant, E_a is the activation energy, R is the universal gas constant, and T is the absolute temperature. Figures 27 and 28 illustrate the temperature dependence of the rate constants.

The alkylation of biphenyl apparently causes the stability of the compounds to decrease as the complexity of the alkyl side chain increases. This observation is in accordance with those of Bolt and Carrol (3, p. 1).

The terphenyls are less stable than biphenyl towards pyrolysis. Fish observed that para-quaterphenyl pyrolysed more readily than the terphenyls (1, p. 5). These observations lead to the conclusion that the pyrolytic stability of nonalkylated polyphenyls decreases as the number of phenyl groups increase. A slight trend in the opposite direction was observed for radiolysis.
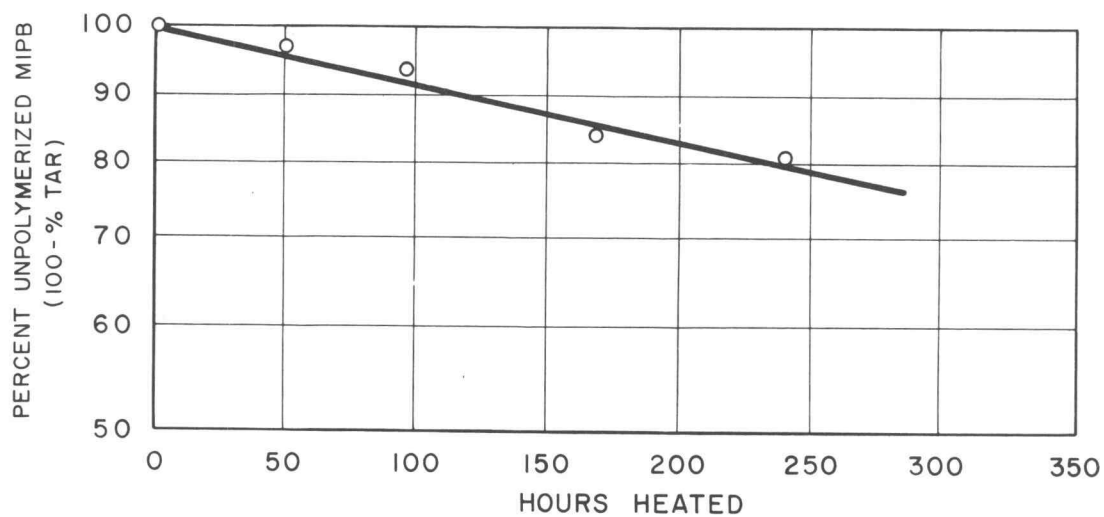
FIGURE 25

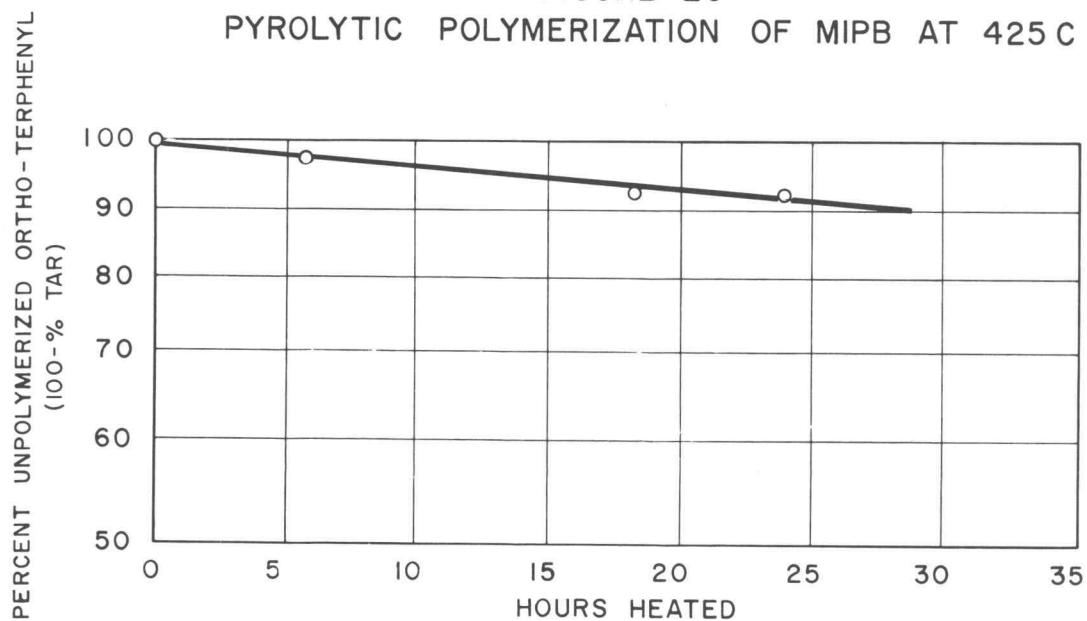PYROLYTIC POLYMERIZATION OF MIPB AT 425 C

FIGURE 26

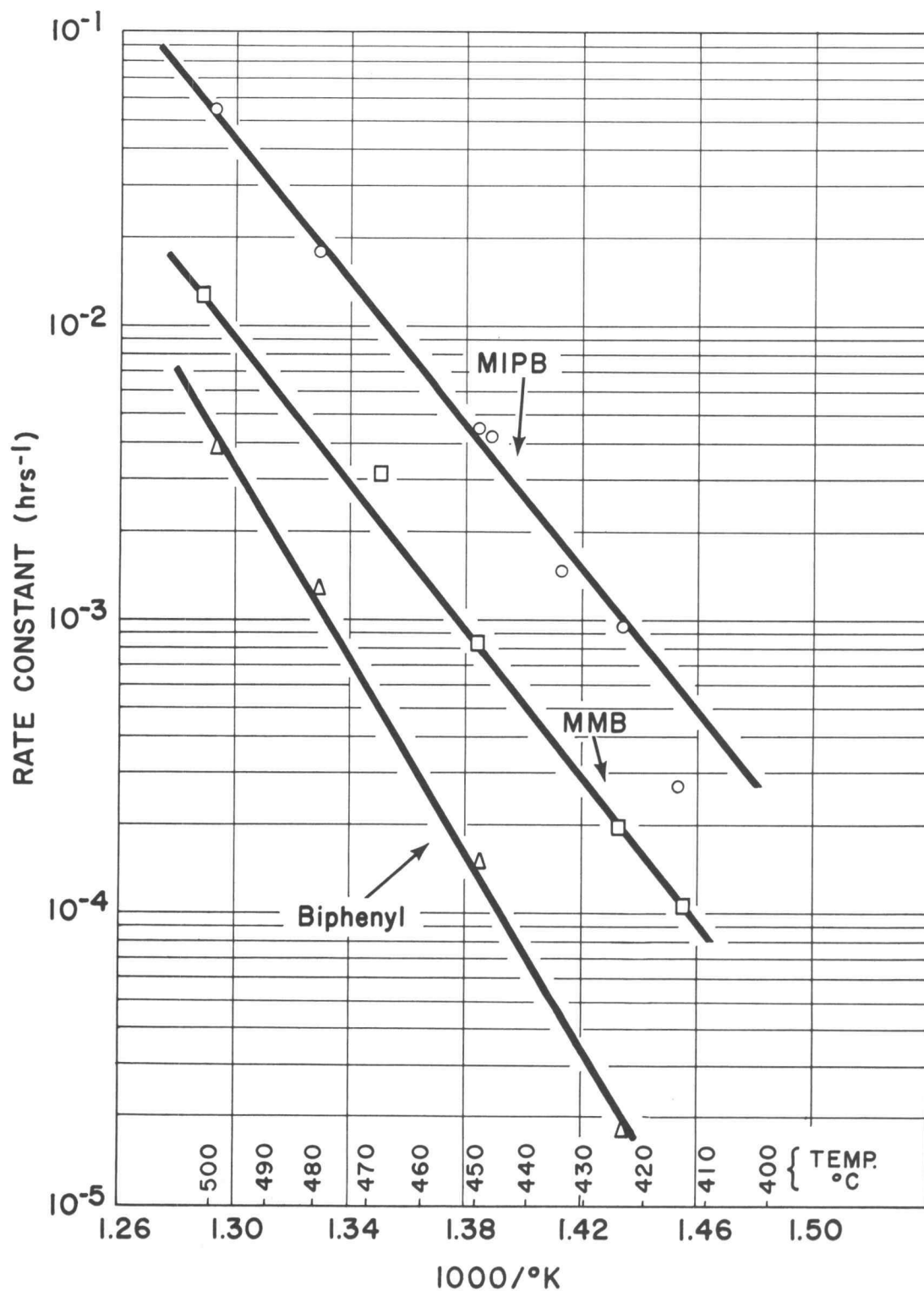PYROLYTIC POLYMERIZATION OF ORTHO-TERPHENYL AT 480 C

FIGURE 27

EFFECT OF TEMPERATURE ON PYROLYTIC POLYMERIZATION
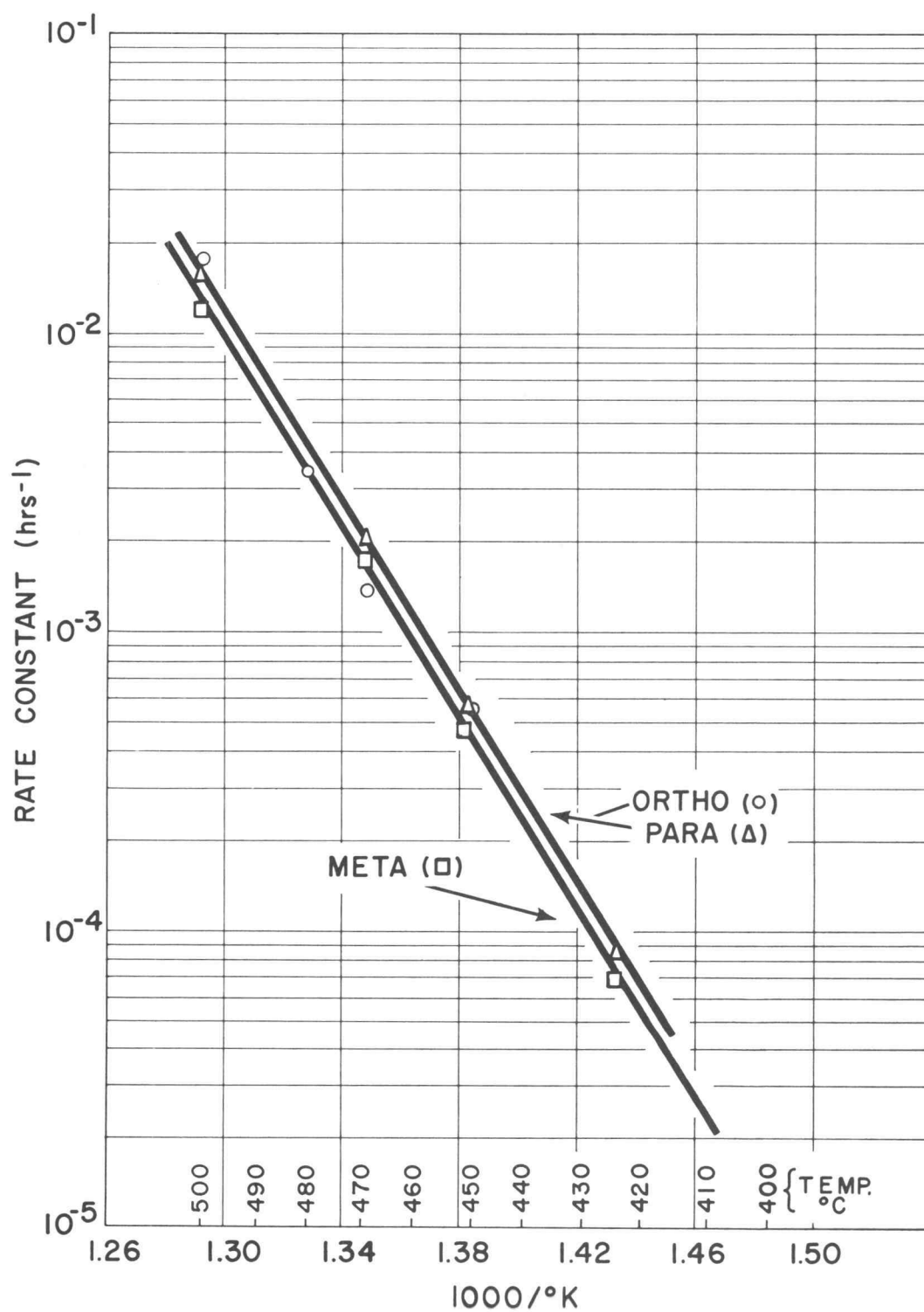RATES, BIPHENYL AND ALKYL-BIPHENYLS

FIGURE 28

EFFECT OF TEMPERATURE ON PYROLYTIC
POLYMERIZATION RATES, TERPHENYLS

AEC-GE RICHLAND, WASH.

The three terphenyl isomers all have about the same pyrolytic polymerization rate. Para-terphenyl polymerized about 25 per cent slower than meta-terphenyl. There is too much scatter in the ortho-terphenyl data to estimate its relative stability with respect to the other two isomers.

The activation energies for the various compounds can be obtained from the slope of the lines in Figures 27 and 28. These values are tabulated in Table 3.

TABLE 3
Activation Energies for Pyrolysis

Compound	Activation Energy
MIPB	56 kcal/mole, ° C
MMB	56 kcal/mole, ° C
Biphenyl	74 kcal/mole, ° C
Terphenyl (all isomers)	72 kcal/mole, ° C

The above observations on the order of reaction are in accord with those of Tilicheev (18). He investigated the pyrolysis of benzene, biphenyl, naphthalene and other condensed ring aromatics, alkylated aromatics, and paraffin hydrocarbons. In each case the pyrolysis reactions were found to proceed according to a first order rate law. His results are reported in terms of total decomposition (that is, the total formation of polymers, unsaturates, gases, etc.) so that his rates are not directly comparable with those reported here. For biphenyl at 500 C (the only available check point) he reports a rate constant for decomposition of 5.8×10^{-2} hr^{-1}. This is about 14 times higher than the rate constant for polymerization at this temperature. This difference seems great, but might be accounted for by the large fraction of low boiling compounds that were formed during pyrolysis.

It is interesting to compare the activation energies measured by Tilicheev with those in Table 3. Because the total decomposition rate would be expected to be about proportional to the polymerization rate, the activation energies for polymerization and decomposition should be approximately the same. However, these activation energies will differ somewhat from those measured for polymerization if there is a change in the types of products with temperature. Tilicheev's measurements were made in a steel reaction vessel.

TABLE 4

Activation Energies for Pyrolysis Measured by Tilicheev

Compound	Activation Energy
Benzene	72 kcal/mole, ° C
Napthalene	93 kcal/mole, ° C
Phenanthrene	99 kcal/mole, ° C

He had measured no activation energy for biphenyl or any alkylated biphenyl.

When the values in Tables 3 and 4 are taken together it is noted that the activation energies seem to fall into three groups. The alkyl-biphenyls have an activation energy of 56 kcal/mole, ° C. This is quite close to the value of 60 kcal/mole, ° C assumed by Tilicheev (on the basis of his work with paraffins) for the pyrolysis of all alkyl benzenes. The pure polyphenyls and benzene have an energy of 72 to 74 kcal/mole, ° C. This number appears to be quite independent of the number of phenyl groups in the polyphenyl compound. The condensed ring aromatics have much higher activation energies, on the order of 90-100 kcal/mole, ° C. These data indicate that the polymerization or decomposition mechanism of the three groups are all different.

COMBINED RADIOLYTIC AND PYROLYTIC DECOMPOSITION

The data on pyrolysis have shown that below 400 C the rate of polymerization is quite slow for polyphenyl compounds (between 0.001 per cent and 0.03 per cent per hour). In a typical reactor coolant system the polymerization rate due to radiolysis would be between 0.1 per cent and 0.01 per cent per hour for polyphenyl coolants (see basis for Figure 29 below).

Data on the effects of heating coolants which were previously irradiated at low temperature indicate that, below the temperature at which pyrolytic polymerization becomes important (i.e., about 400 C), the radiolytic rate is not greatly affected by temperature. The only effect to be expected in this intermediate temperature range is a slight decrease in rate due to pyrolytic degradation of the tars. Capsule irradiation data by Woodley (21) in the same reactor as the experimental loop are in accord with this hypothesis. Rate constants have been calculated from Woodley's data and have been corrected to the same flux conditions as those in the low temperature loop. The data are compared in Table 5.

TABLE 5

Comparison of Radiolytic Polymerization Rates Below 400 C

	Rate Constants (1 mev neutrons/cm^2)$^{-1}$		
	Woodley's Capsule Data		Loop Data
Compound	50 C	330 C	100 C
MIPB	1.8×10^{-18}	1.3×10^{-18}	2.0×10^{-18}
MMB	1.3×10^{-18}	1.1×10^{-18}	----
Biphenyl	1.0×10^{-18}	1.6×10^{-18}	1.8×10^{-18}

With the exception of the results on biphenyl; it is seen that the effect of increasing the irradiation temperature to 330 C is to slightly decrease the polymerization rate. Woodley's biphenyl analyses are

of somewhat doubtful validity since the tar contents were obtained by distillation analysis at a time before the procedure for biphenyl was well worked out. The loop biphenyl samples were analyzed by a combined distillation and infra-red technique.

The agreement between the rate constants measured in the small capsule irradiations, and those measured in the recirculating loop is quite good. This attributes to the validity of the rate equation for polymerization in a recirculating system for expressing the rate in a manner that is independent of irradiation geometry.

Based on the above observations, it can be concluded that the polymerization rate in a reactor system will remain almost independent of temperature until a transition temperature is reached, where the pyrolytic damage becomes significant with respect to radiolytic damage. The hypothesized occurrence of these transition temperatures is illustrated in Figure 29. Because the radiolytic rates of all polyphenyl compounds studied (MIPB, biphenyl, ortho-, and meta-terphenyl) vary only about 20 per cent between each other, only the radiolytic rate of MIPB (irradiated at 100 C) is plotted. This MIPB rate will be somewhat too high for the temperatures at which it is plotted, because no allowance was made for the slight decrease in radiolytic rate at these higher temperatures. The epithermal (1 mev) flux was taken at a typical value of 10^{12} neutrons/cm^2, sec, and the in-flux to total volume ratio is one to ten.

The transition temperatures from Figure 29 are tabulated below.

TABLE 6

Transition Temperatures

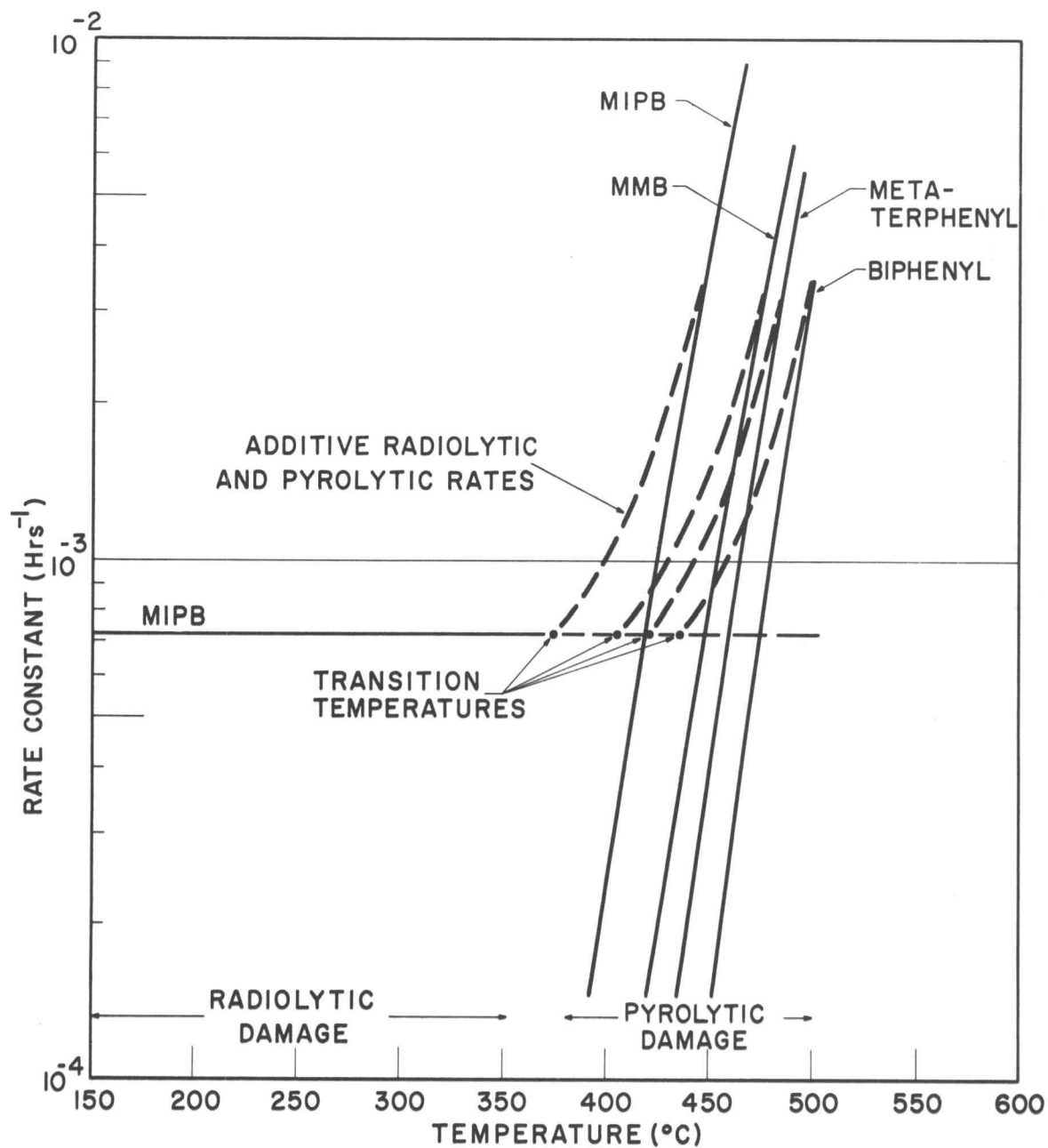| Compound	Temperature
MIPB	370 C
MMB	400 C
Terphenyls (all isomers)	420 C
Biphenyl	430 C

FIGURE 29

COMBINED RADIOLYTIC AND PYROLYTIC POLYMERIZATION

From a practical standpoint there is an advantage to operating a reactor so that the coolant temperature is below the transition temperature so as to minimize decomposition. In a reactor system such that the radiolytic polymerization rate is different than that chosen as an example in Figure 29; the transition temperatures would be somewhat altered because of the change in position of the horizontal portion of the curves. If the acceptable decomposition rate is above that resulting from radiolytic polymerization, the reactor coolant temperature can be above the transition temperature.

CONCLUSIONS

The primary reaction kinetics of the radiolytic and pyrolytic decomposition of several polyphenyl compounds have been established under a variety of conditions. At temperatures on the order of 100 C or less the polymerization is only dependent on the amount of unpolymerized material present (first order law). Between about 100 C and 400 C the rate law is still primarily of first order, but contains a term to correct for pyrolytic degradation of the polymer. Above about 400 C the pyrolytic action is the predominating factor. Here again, pyrolysis is found to go according to a first order rate law.

The common procedure for determining the maximum utilizable temperatures for a new coolant involves making high temperature irradiations (usually in capsules) in a reactor. This type of experimentation requires complicated instrumentation and controls. The rate laws derived above bring out an important aspect of these experiments. Unless the irradiations are done at several temperatures (and actually straddle the transition temperature), the maximum utilizable temperature cannot be found. It will also be difficult to interpret the results of the capsule irradiations if they are made in the transition range, since a combined radiolysis and pyrolysis is observed.

The evaluation of a new polyphenyl coolant can be greatly simplified if the rate laws are assumed to hold for all polyphenyl compounds. The transition temperature, which is directly related to the maximum utilizable temperature, can be estimated with the data from only a few measurements. One low temperature irradiation is required to establish the radiolytic polymerization rate, and two to three pyrolysis experiments, done in the laboratory, are needed to establish the pyrolytic rate.

Another important contribution of the rate laws is that they provide a means for accurately comparing the stability of several compounds on the same basis (that is, by comparing rate constants). This same observation holds true in making comparisons of the effects of various types of destructive irradiation on the same compound.

The last important aspect of these studies is that they point out that the only reliable means of measuring coolant decomposition is by measuring tar content. Gas pressure build-up and viscosity changes are as susceptible to changes in experimental temperature conditions as they are to the amount of polymerization that has occurred. Modifications of the infra-red absorption spectra are also sensitive to temperature. On the other hand, the tar concentration measurements give directly the rate of disappearance of unpolymerized reactor coolant.

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