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HEAVY WATER ORGANIC COOLED REACTOR

MELTING POINTS, TRANSITION ENERGIES, AND SPECIFIC HEATS OF POLYPHENYL REACTOR COOLANTS

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ABSTRACT

Differential scanning calorimetry, a relatively new quantitative technique for making direct calorimetric measurements, has been applied to studies of the melting behavior, transition energies, and specific heat of polyphenyls which are of interest to organic coolant technology in the Heavy Water Organic Cooled Reactor program. The apparatus (Perkin-Elmer DSC-1) was used to determine melting points and heats of fusion of the major constituents of polyphenyl coolants, namely, biphenyl, ortho-, meta-, and para-terphenyl. The melting characteristics of two synthetic terphenyl binaries similar to proposed HWOCR coolants (ortho-meta isomer ratios of 2:1 and 1:2) were studied with respect to the effect of the high boiler (HB) fraction of the radiolytic and pyrolytic decomposition products and of para-terphenyl on the melting transition range. The effect of HB addition on the two binary mixtures is both time and concentration dependent in that the observed crystallinity of the samples decreases with increased HB addition, and increases with time. The addition of para-terphenyl to both binary mixtures, with and without HB, increases their final melting point. The calorimetric capabilities of the instrument were also utilized in the measurement of the specific heats of solid biphenyl, ortho-, and para-terphenyl.

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I. INTRODUCTION

Organic coolants were first used in nuclear reactors in the United States in the Organic Moderated Reactor Experiment (OMRE), Idaho Falls, Idaho, during its operation from 1957 to 1963. They have been used subsequently in the Piqua Nuclear Power Facility (PNPF) Piqua, Ohio, since June 1963, and have been chosen as possible coolants for the U.S. Heavy Water Reactor Development program. Organic coolants offer a number of important advantages including higher temperatures at lower pressures than water, and compatibility with reactor structural materials and nuclear fuels. Organic coolants used in nuclear reactors in this country are commercial mixtures of terphenyl isomers which possess a high degree of temperature and radiation stability coupled with availability and low cost. An important consideration in the use of terphenyls as coolants in the Heavy Water Organic Cooled Reactor (HWOCR) program is their liquidus temperature (final melting point), since the coolant must be completely liquid at the maximum temperature of the heavy water moderator, i.e. 200°F.

The major objective of this study was to supply data on the melting characteristics of terphenyls and terphenyl mixtures which are important to the HWOCR concept. Conventional methods, such as the Fischer-Johns technique, rely on visual observation of the melting point. With such techniques it is difficult to obtain accurate final melting point data for irradiated coolants that may range in color from a light amber to an opaque dark brown or almost black material. Differential scanning calorimetry is unaffected by the optical properties of the sample since it records energy changes and temperatures associated with the melting of crystalline material. It can also be used to measure specific heats of solid materials. The results of the measurements made with this instrument are described in this report.

Santowax, trade name of Monsanto Chemical Co., St. Louis, Mo

II. EXPERIMENTAL

A. APPARATUS AND MEASUREMENT TECHNIQUE

The Perkin-Elmer Model DSC-1 Differential Scanning Calorimeter is a relatively new instrument for performing differential thermal analyses. The operating principle of the instrument is illustrated in a schematic diagram in Figure 1. The schematic system is most easily understood if it is divided into two separate "control loops," one for average temperature control, the second for differential temperature control. In the average temperature loop, a programmer provides an electrical output signal which is proportional to the desired temperature of the sample and reference holders in the sample holder assembly. The programmer temperature information is also relayed to the strip chart recorder and appears as the abscissa scale marking. The programmer signal, which reaches the average temperature amplifier, is compared with signals received from platinum resistance thermometers permanently embedded in the sample and reference holders via an average temperature computer. If the temperature called for by the programmer is greater than the average temperature of the sample and reference holders, more power will be fed to the heaters, which, like the thermometers, are embedded in the holders. If the average temperature is lower than that demanded by the programmer, the power to the heaters will be decreased. In the differential temperature control loop, signals representing the sample and reference temperatures, measured by the platinum thermometers, are fed to the differential temperature amplifier via a comparator circuit which determines whether the reference or sample signal (temperature) is greater. The differential temperature amplifier output will adjust the differential power increment fed to the reference and sample heaters in the direction and magnitude necessary to correct any temperature difference between them. A signal proportional to the differential power is also transmitted to the pen of the galvanometer recorder. The direction of the pen excursion will depend on the direction of excess power input (sample or reference heater).

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Figure 1. Block Diagram of DSC-1 Differential Scanning Calorimeter

The recorded results of an analysis on the DSC-1 are illustrated in Figure 2, using one of the metal samples furnished as a calibration standard for the instrument. The abscissa represents temperature as recorded by the first pen marker; with the Leeds and Northrop Speedomax 2-pen recorder used, each mark equals one degree Kelvin, with a skip of the marker every decade. A write-in of the reference temperature obtained from the digital dial display allows for simple derivation of all subsequent temperatures during a scan. The second pen draws a "baseline" which represents a condition in which no transitions are in progress; it also periodically "peaks" indicating the transitions of the sample material, in this case indium. The information derived from the thermogram includes: (1) the temperature at which a transition occurs, indicated by the start of the deflection from the baseline; (2) the endothermic or exothermic nature of the transition, indicated by the direction of the excursion of the pen from the baseline; and (c) the energy absorbed or liberated in a transition, indicated by the area under a peak.

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Figure 2. Fusion and Crystallization
of Indium

The major components of the apparatus, exclusive of the potentiometric 2-pen recorder, are shown in Figure 3. The control or programmer unit has a digital counter which displays the temperature of the calorimeter in $^{\circ}\text{K}$. Below the dial is a handwheel which allows for manual setting of temperature from 173 to 723 $^{\circ}\text{K}$ (-100 to +500 $^{\circ}\text{C}$). The scanning speed can be varied with the Scan Speed control from 0.625 to 80 $^{\circ}\text{C}/\text{min}$. Sensitivity of scan is selected with the "Range" control. Sensitivities of 2 to 32 millicalories per second for half-scale deflections on the 5-milliamp recorder may be obtained. Lower ranges are used for measuring weak transitions or where small samples are used. The lever switch actuates the programmer and starts the temperature scan at the rate and range previously selected. The scan may be either to higher or lower temperatures. The neutral position permits manual changes in temperature or maintenance of isothermal conditions. The slope control is used only to compensate for differences in variation in thermal dissipation properties of the sample and reference holders, which would otherwise tend to produce a sloping baseline. The zero control is used to position the pen in the recorder at the desired "baseline" level. The analyzer section shown includes

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Figure 3. Control Unit and Analyzer
of the DSC-1

the average and differential temperature controls used for calibration. The sample holders accommodate an aluminum sample container which has an ID of 6.5 mm and a depth of 1.5 mm.

The specific heat measurements were made using the DSC-1 with two aluminum sample holder covers, two sapphire (aluminum oxide) disc standards of different sizes, and a calibration chart giving the specific heat of aluminum oxide (in the form of synthetic sapphire or corundum) from 0 to 1200°K. Sample pans used for both the melting transition and specific heat measurements were furnished with the instrument, and consisted of aluminum rimmed discs and covers made to fit inside the sample holders in the sample holder assembly. After insertion and weighing of samples in the aluminum pans, they were encapsulated by means of a special press furnished for this purpose. The encapsulation does not completely seal the organic sample in the capsule. Some vaporization or sublimation out of the capsule does occur at higher temperatures, particularly for liquid samples where volume increases with temperature. Since para-terphenyl has a significantly higher melting point and sublimation pressure than the ortho-, and meta-terphenyl, a fine, sealed Pyrex capillary (covered with aluminum foil) was used for the melting point and heat of fusion measurement. The imperfect seal of the sample in the aluminum containers

also created another problem. This problem, discussed previously,⁽¹⁾ can be traced to changes in thermal emissivity caused by the partial pyrolysis of exuded organic material onto the top of the covered sample container. In some cases this can cause very significant variations in the normal base line. It was found that this effect could be minimized by placing aluminum covers over the pan supports.

The atmosphere around the sample holder assembly must be purged with inert gas to flush out decomposition products which might foul the sample holder assembly. For this purpose nitrogen was used at a flow rate of ~30 ml per minute.

Measurements of transition peak areas were made with a Keuffel and Esser compensating polar planimeter.

B. MATERIALS

The important constituents of the organic coolants of interest to the HWO CR concept are the polyphenyl compounds biphenyl, ortho-, meta-, and para-terphenyl. For the commercially available coolants which are under consideration for use in the HWO CR at present, ortho- and meta-terphenyl may be considered the major components, with biphenyl and para-terphenyl the minor ones. Para-terphenyl, which is the highest melting terphenyl isomer (485°K), has a significant effect on the final melting point of ortho- and meta-terphenyl mixtures. Studies of these mixtures and the effect of para-terphenyl content (and HB) were therefore of major importance in this investigation. The biphenyl, ortho-, meta-, and para-terphenyl used in the experiments were Eastman White Label grade materials. The biphenyl, ortho-, and para-terphenyl had an initial purity of 99.5⁺% and were further purified by sublimation. The meta-terphenyl used consisted of the "as-received" material, and also a sample of lower para-terphenyl content prepared by elution with cyclohexane through high-grade alumina. A comparison of the para-terphenyl content in the two samples by infrared spectrometry indicated 4.5% and 1.1% para-terphenyl in the "as-received" Eastman White Label grade and purified sample, respectively. For determination of the effect of the high boiler fraction (HB), which is the major decomposition product formed when the terphenyl mixtures

are irradiated, a sample was used which had been separated from irradiated OM coolant* by distillation.

Materials used as calibration standards included both inorganic and organic compounds. Calibration materials furnished by Perkin-Elmer included tin, lead, and indium metals as standards. Organic materials included reagents with certified micro-melting points⁽²⁾ covering a temperature range of 317 to 681°K.

*Coolant in the U-3 Loop, NRU Reactor, Chalk River, Ontario, Canada. The HB content of the coolant was ~22%.

III. RESULTS AND DISCUSSION

A. MELTING TRANSITION MEASUREMENTS

Thermograms of the melting transitions of biphenyl and the three terphenyls are shown in Figure 4. The para-terphenyl peak shown is shorter in amplitude and also somewhat broader at the base than for the others because the sample was sealed in a small Pyrex capillary to prevent sublimation and partial loss of the sample, as mentioned previously. The melting points were obtained by noting the point of initial deflection of the baseline for a number of samples of each compound. The heats of fusion were obtained by drawing a baseline across the bottom of each peak, measurement of the peak area with a planimeter, and calculation of the heat of fusion either by: (1) comparison with a material of known transition energy (e.g., indium) under the same conditions, or (2) measurement of the rectangular area with the planimeter which is equal in width to one half of the chart (full scale), and in length equal to one minute of run. The data for the four polyphenyls are summarized in Table 1. The melting points are in agreement ($\pm 1^\circ\text{K}$) with data given in the literature⁽³⁾.

Figure 4. Melting Transitions of Some Polyphenyls (Range 4; Scan $10^\circ/\text{min}$; Chart Speed 1 in./min)

TABLE 1
MELTING POINTS AND HEAT OF FUSION OF POLYPHENYLS

Compounds	Melting Point (°K)	Heat of Fusion (cal/gm)
Biphenyl	342 ± 1	28 ± 1
Ortho-Terphenyl	330 ± 1	18 ± 1
Meta-Terphenyl	360 ± 1	25 ± 1
Para-Terphenyl	485 ± 1	35 ± 1

The heats of fusion for biphenyl, ortho-, and meta-terphenyl are in good agreement with recent experimental data. No previous measurements for heat of fusion of para-terphenyl are available for comparison. The melting behavior of meta-terphenyl is worthy of some discussion. Repeated melting and freezing of the same sample resulted in a lower melting point (350-352°K) at least 50% of the time for as many as 13 cycles. This was the case for both the low (1.1%) and high (4.5%) para-terphenyl samples. The phenomenon was also observed when a Fischer-Johns melting point apparatus was used. In previous studies of the melting mechanism of polyphenyls⁽⁴⁾, it was noted that the volume increase in melting is largest for the linear polyphenyls (biphenyl and para-terphenyl), and smallest for branched molecules (ortho-, and meta-terphenyl). Furthermore, on cooling the melts, a measured viscosity increase was observed as the melting point was approached, which was interpreted as being due to the formation of interlocked clusters of molecules or "cybotactic" groups. This behavior was particularly marked for ortho-terphenyl, and to a somewhat lesser extent, for meta-terphenyl. Since these two also show the most pronounced tendency to supercool (the ortho- more than the meta-terphenyl), it is concluded that the clusters formed on melting appear to differ in average structure and properties from the more ordered molecular aggregates which can act as "crystal nuclei." One can only speculate as to whether the interlocked molecular aggregates can act as crystal nuclei leading to an unstable crystalline state, which at some point later in time undergoes a rearrangement to the normal melting crystalline state. The observed phenomenon is largely of academic interest, especially so when considered in connection with the irradiated materials which contain a wide variety of decomposition products in addition to the terphenyls.

The melting characteristics of ortho-, meta-terphenyl mixtures over the range from the meta-rich (1:6 OM ratio) to the ortho-rich (5:1 OM ratio) were examined briefly to determine the approximate eutectic ratio. The results shown in Figure 5 indicate that the eutectic is close to the 2:1 OM ratio previously reported.⁽⁵⁾ A sharp initial eutectic peak is seen in the meta-rich region in the thermogram, which is probably the OM eutectic. This peak is then followed by the more gradual melting of the meta-terphenyl. The melting range narrows noticeably as the 2:1 OM ratio is approached, and becomes broader and distorted as the mixture becomes more ortho-rich. The ortho-rich mixtures, however, show a lower melting range than the meta-rich mixtures. The majority of the melting studies were performed using the two OM ratios which were of more immediate interest to the HWOCR program, namely the 1:2 and 2:1 OM ratios, in order to evaluate the effect of high boiler and para-terphenyl addition on their melting characteristics.

Figure 5. Thermograms of Synthetic OM Mixtures

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The effects of addition of high boiler (HB) to 1:2 ratio ortho-, meta-terphenyl (OM) mixtures (using the low, or 1.1% para-terphenyl-in-meta-terphenyl) are shown as composite thermograms in Figures 6 and 7. Thermograms determined within 1 to 2 hr after the samples are prepared, (Figure 6), show an almost complete absence of the first, or eutectic, peak in the 5 and

10% HB samples. After a time lapse of about 2 weeks (Figure 7), the initial eutectic, peak is prominent in the 5% HB sample, but is still absent in the 10 and 20% HB samples. Pertinent data from Figure 7 are summarized in Table 2. It is noted that for the 5% HB level the reduction in crystallinity (or the melting transition energy of the HB-containing sample relative to the pure parent product) is very marked, even after standing for two weeks.

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Figure 6. Effect of HB on Synthetic 1:2 OM Mixtures (1-2 hr after preparation)

Figure 7. Effect of HB on Synthetic 1:2 OM Mixtures (About 2 weeks after preparation)

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TABLE 2
EFFECT OF HB ADDITION ON MELTING TRANSITIONS - SYNTHETIC
1:2 OM MIXTURES (~2 WEEKS AFTER PREPARATION)

Added (%)	Transition (°K) Temperature		Transition Energy (cal/gm)	Crystallinity* (%)
	Initial	Final		
0	311	356	21.1	100
5	303	349	11.0	52
10	304	350	10.5	49
20	304	343	9.3	44

*Defined as the ratio of the Transition Energies of the sample containing HB to the pure terphenyl mixture.

Two weeks after preparation, the initial melting point shows a relatively constant reduction of 7 to 8°K with increasing HB content; the final melting point decreases by 7°K at 5% HB to 13°K at 20% HB. The crystallinity decreases also but the decrease is not a linear function of HB content. Three weeks after preparation, the crystallinity of the 5% HB sample has increased to 80%, and the 10% HB sample shows no change at 49% with the initial eutectic peak still absent.

The effect of added para-terphenyl to 1:2 OM mixtures is shown in Figure 8. These OM mixtures were prepared from Eastman grade meta-terphenyl containing 4.5% para-terphenyl. Figure 8 illustrates the difficulty which arises in evaluating melting transitions of samples containing low concentrations (up to 10%) of para-terphenyl in OM mixtures. Note that the para-terphenyl transition is gradual, and relatively small by comparison with the major transition zone. At these low para-terphenyl concentrations it is difficult to accurately describe the final temperature of the para-terphenyl transition. The same problem exists for the case of the 1:2 OM samples containing 10% HB, to which para-terphenyl has been added. Figure 9 illustrates thermograms of these latter samples, run approximately three months after initial preparation. The para-terphenyl transition, as shown by the flat plateau following the major transition, is again relatively small compared to the major

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Figure 8. Effect of Added Para-Terphenyl on Synthetic OM Mixtures

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Figure 9. Effect of Added Para-Terphenyl on Synthetic OM Mixtures Containing 10% HB

transition. The major problem is that of limitation of sample size (<20 mg for powdered or semi-solid material) and the relatively small amount of para-terphenyl initially present. Even with these limitations, it is possible to establish a general relationship of liquidus temperatures as a function of para-terphenyl content in OM mixtures containing 0-10% HB.

For the synthetic 2:1 OM mixtures (using the low or 1.1%, para-in-meta-terphenyl) the effect of HB content, up to 10%, is shown in Figure 10. This run was made about three weeks after preparation of samples. The 2:1 OM mixtures have a very high tendency to supercool. As reported in the Canadian literature, ⁽⁶⁾ this supercooled state sometimes persists over a period of months. As shown in the figure, at the 10% HB concentration, the initial melting point drops from 310 to 302°K, with very little effect on the termination of the transition. The crystallinity, as defined previously, has decreased by about 35%, at the 10% HB level. The effect of para-terphenyl on the synthetic 2:1 OM mixture (Eastman grade meta-terphenyl used) is illustrated in Figure 11.

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Figure 10. Effect of HB on Synthetic 2:1 OM Mixture (About 3 weeks after preparation)

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Figure 11. Effect of Para-Terphenyl on Synthetic 2:1 OM Mixtures

As in the case of the 1:2 OM data shown previously, in the region of interest, the para-terphenyl transition is gradual and small. Some distortion of the major OM eutectic peak is apparent even though aluminum covers were used over the heater cavities. This distortion apparently increases as sample size increases to above 20 mg. The effect of para-terphenyl addition on 2:1 OM samples containing 10% HB is shown in Figure 12. This run was made after a time lapse of three months. The aluminum covers over the sample heater cavities were used to reduce emissivity effects. The para-terphenyl transition is discernible, but again is relatively small in the region of interest.

In order to establish the concentration of para-terphenyl in OM coolants which coincides with a maximum liquidus temperature of 200°F, the final melting points from the various thermograms were replotted and shown in Figure 13. The 2:1 and 1:2 OM ratio mixtures have been plotted together. Two curves have been drawn through the sets of points, one for 0% HB and the other for 10% HB. While the data are scattered, it is seen that no systematic difference in the liquidus temperature is observable for the two OM ratios. If

Figure 12. Effect of Para-Terphenyl Addition on Synthetic 2:1 OM Mixtures Containing 10% HB

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Figure 13. Effect of Para-Terphenyl Content on the Liquidus Temperature for OM Mixtures

the HWO CR contract had been continued, further work was indicated in the 0.5 to 3% p-terphenyl range without added HB in order to more accurately define the coolant specification on p-terphenyl. The practical application of the curve shown for the condition of "OM with 0% HB" is for the initial coolant loading of a reactor. No HB would yet have been produced by the reactor. The maximum para-terphenyl content for the initial reactor coolant is 2.1%. The curve shown for OM with 10% HB is for the condition of the steady-state operating

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Figure 14. Typical Specific Heat Determination

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Figure 15. Specific Heat of Solid Biphenyl, Ortho-, and Para-Terphenyl (Smoothed data)

reactor coolant in the event of reactor shutdown. For this case, the maximum para-terphenyl content to stay below a liquidus temperature of 200°F is 4.1%.

B. SPECIFIC HEAT MEASUREMENTS

The DSC-1 was used to measure the specific heat of the polyphenyls. This procedure is an extension of the basic function of the calorimeter, which is to measure the amount of heat required to raise the temperature of a sample at a predetermined rate. The ordinate read-out is directly proportional to the heat capacity dH/dT . For a 1-gram sample, this is the specific heat at constant pressure, c_p , in calories per gram per degree. In the determination, sapphire is used as an external standard for which accurate heat capacity data are available.⁽⁷⁾ The method consists of scanning the sapphire standard over the desired range, making a blank determination, and then scanning the sample over the desired range ($\sim 10^\circ\text{K}$). The blank deflection at the temperature at which the specific heat is determined is then added or subtracted from the sapphire and sample deflections. Thermograms of sample, sapphire, and blank would appear as indicated in Figure 14, showing the measurement of the amplitude of the three respectively at the desired temperature. Results of measurements of the specific heat of biphenyl, ortho-, and para-terphenyl are shown

in Figure 15. Results for biphenyl, for which some previous experimental data are available⁽⁸⁾, show good agreement.

The applicability of the DSC to measurement of C_p of coolant samples in the liquid phase region at higher temperatures is dependent on use of a container which can be effectively sealed to prevent vaporization of samples. Such a container was not available at the time these measurements were made.

IV. SUMMARY AND CONCLUSION

It has been shown that differential scanning calorimetry can be used to obtain melting points and transition energies of the pure terphenyl compounds. The method has also been used to evaluate the individual and combined effects of HB and para-terphenyl on ortho-, and meta-terphenyl binary mixtures. There is a reduction in degree of crystallization (or crystallinity) when HB is added up to 10% to 1:2 and 2:1 OM mixtures. This effect is time dependent; i.e., there is a gradual increase in crystallinity with time.

The melting range of OM mixtures, with and without HB, is greatly increased by the addition of para-terphenyl. It was found that the final melting point is essentially independent of the OM ratio in the mixture; 10% HB suppresses the melting point of such mixtures slightly. The maximum para-terphenyl content in OM mixtures without exceeding the 200°F melting point is 4.1% for coolant containing 10% HB, and 2.1 for coolant containing no HB.

The applicability of DSC to the determination of specific heats of pure, solid polyphenyl has been demonstrated. Its future use for coolants in the liquid phase region should be possible but is dependent upon use of a suitably sealed sample container.

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