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By

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INTRODUCTION

The objective of the research under this contract is the preparation of polymers which can be made into films for use in capacitors. Theoretical studies have indicated that the anthracene nucleus should impart beneficial electrical properties. The work has been divided into two phases:

- (1) The preparation of 9,10-disubstituted anthracenes which can undergo condensation polymerization. The previously developed routes involved 9,10-dichloromethyl-anthracene, a potent allergen.
- (2) The preparation of condensation polymers for evaluation as capacitor films.

SUMMARY OF RESULTS

(1) It has been observed that polyesters derived from anthracene-9,10-dipropionic acid and various simple glycols are of fairly low molecular weights and soften in the range 100-160°C. When purified polyester is heated above its melting point, "curing" takes place and the softening point rises to 200-300°C. Unfortunately, the "cured" polymers are extremely brittle.

(2) A sample of hexamethylene anthracenedipropionate (m.p. 166-8°C) was molded at 188°C and 3500 psi into a film 0.025 inch thick which adhered tightly to the aluminum foil used to line the mold. This sample had a dielectric constant of 2.66 at 1 megacycle (measured by Mr. Dale Grimes of the Electrical Engineering Department).

(3) In an effort to improve the brittleness several polymers were made from the dipropionic acid and various polyethylene glycol (MW 400-3000). All were soft and sticky and those made from the larger polyglycols were somewhat water-soluble.

Since "Mylan" (polyethylene terephthalate) forms good electrical films, a copolymer of equivalent quantities of methyl terephthalate and methyl anthracenedipropionate with a 10% molar excess of ethylene glycol was prepared. The resulting polymer was sticky, perhaps as a result of experimental difficulties.

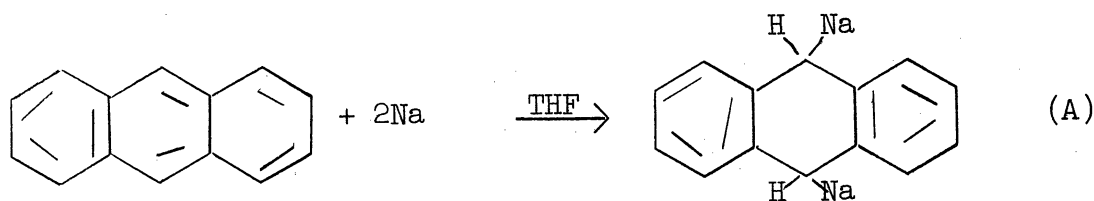
A similar experiment in which the terephthalic ester was replaced by dimethyl sebacate, and ethylene glycol by hexamethylene glycol was much more encouraging. The polymer appeared to be extremely tough and flexible; a larger sample is being prepared for electrical testing. It is hoped that the gain in toughness and flexibility was not at the expense of the electrical properties.

(4) As a simplification of the preparation of polymers from the dipropionic acid some effort was devoted to using the diacid directly, instead of its ester, with zinc chloride catalysis. In a number of runs the yields of inferior polymers were lower with the acid; the ester method will be retained.

(5) All samples of polyamides obtained from the dipropionic acid and several diamines were extremely insoluble in common solvents (including dimethylformamide) and had such high melting points ($> 300^{\circ}\text{C}$) that it seems improbable that any practical use could be made of them as capacitor films. Perhaps use of a propylene diamine or ethanolamine would produce more tractable materials. Limited manpower does not permit the investigation of this possibility; therefore, concentration will be on the polyesters.

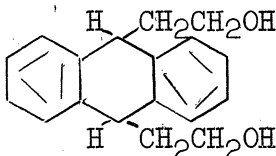
(6) An all-hydrocarbon anthracene-based polymer was prepared by a Wurtz-type reaction between sodium dispersion and dichloromethylanthracene. Two fractions were obtained: (a) soluble in chloroform, melts at $175\text{-}185^{\circ}\text{C}$, chlorine-free, and (b) insoluble in tetrahydrofuran, darkens and shrinks at 245°C , but does not melt to 300°C , and contains a trace of chlorine. Tests are being conducted on these materials.

(7) A broad program exploring the synthetic utility of 9,10-disodio-9,10-dihydroanthracene (A) has given some encouraging results, but mostly otherwise.



The following reactions of (A) were tried:

a. With ethylene oxide reported by Mikhailov. Our properties than he reported;



was expected, previously product has different prop- analyses are pending.

b. With propylene oxide the product should be $AH_2(CH_2CHOHCH_3)_2$. It has been possible to obtain solid products by molecular distillation, but they have not yet been identified. It is hoped to degrade the side chain to $-CH_2COOH$ with hypochlorite and to convert it to $-CH_2CH_2COOH$ through the Willgerodt reaction.

c. With benzalacetophenone the expected compound is $AH_2(\overset{\phi}{CH}CH_2CO\phi)_2$. Two different products were isolated in low yield, but neither analyzed correctly for the expected product nor the mono addition compound $AH_2\overset{\phi}{CH}CH_2CO\phi$.

d. With ethyl bromoacetate and ethyl iodoacetate none of the expected mono or diacetic ester was obtained. Some dihydroanthracene was isolated, but the major product was a dark oil which could not be purified.

e. With allyl chloride the expected $AH_2(CH_2CH=CH_2)_2$ may be present in the oil obtained. It is hoped that the presence of the desired compound can be shown by an infrared spectrum and by formation of a derivative with 2,4-dinitrobenzenesulfonyl chloride.

f. With β -propiolactone no product corresponding to $AH_2(CH_2CH_2COOH)_2$ was found. Instead, the acidic material was a sticky gum, probably polymerized lactone, and an odor of ethylene from lactone decomposition was detected.

g. With benzoyl chloride $AH_2(CO\phi)_2$ was expected. Considerable anthracene was recovered, but the remainder is an oil.

h. With acrylonitrile $AH_2(CH_2CH_2CN)_2$ was predicted. This has not been obtained in several trials, although considerable dihydroanthracene was recovered and often polyacrylonitrile.

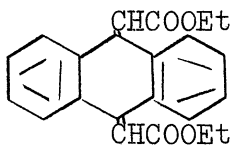
(8) Speculation as to the reasons for the lack of success in 7 is divided in two classes:

a. The reactions postulated may have gone as expected, but since a compound of the type AH_2X_2 can exist in stereoisomeric forms, the mixture might well be difficult to crystallize. Dehydrogenation would give non-stereoisomeric anthracene derivatives which might be more readily purified. Due to the time limitation this has not been attempted, but it will be tried before abandoning the synthesis. A further difficulty may be caused by the probable presence of a mono substituted dihydroanthracene; it was observed in carbonating the solutions of (A) that some mono acid was found.

b. Organosodium compounds are frequently such strong bases that their nucleophilic properties are overshadowed by their tendency to abstract hydrogen and to effect condensations. Morton has provided many examples with amylsodium. Although (A) is much less basic than $C_5H_{11}Na$ (the former does not cleave the ether solvent rapidly) the isolation in many examples in 7 of dihydroanthracene provides evidence that this hydrogen abstraction is prominent.

c. It is believed that use of dilithiodihydroanthracene instead of (A) would minimize the difficulties described in 8b, since the former would be equally nucleophilic, but much less basic. The work to date has been concerned with the sodium adduct of anthracene, since (1) sodium adds much more readily than lithium, (2) sodium is cheaper, and (3) sodium (m.p. $97^\circ C$) is very readily dispersed in an inert solvent, but lithium (m.p. $186^\circ C$) would be much more difficult and a new technique would have to be developed.

(9) A Reformatsky reaction on anthraquinone gave a product which may be



EXPERIMENTAL DETAILS

(1) A sample of hexamethylene anthracenedipropionate was placed in an oven. At $100^\circ C$ it flowed slowly into a hard continuous film and darkened. On storing for 3 days at $185^\circ C$ the film was extremely brittle with a melting point of $360^\circ C$; it melted over a flame, however.

A sample of ethylene anthracenedipropionate flowed at $100^\circ C$ into a soft film and darkened. After 3 days at $185^\circ C$ the now brittle film softened at about $320^\circ C$.

Preparation of Polyesters

(2) The polyesters described in sections 2 and 3 of the Summary were prepared by the following general method. The glycol and dimethyl anthracene-9,10-dipropionate were charged into a sidearm test tube fitted with a capillary reaching to the bottom. A small amount of litharge (PbO) was added and the mixture was refluxed for 1 hour, then placed in a bath at $180^\circ C$. A slow stream of dry nitrogen was bubbled through for 1/2 hour to entrain the methanol; the residue was pumped at 2 mm and $200-220^\circ C$. Finally, the contents of the tube were washed out with chloroform, filtered, and the polymer was precipitated with a large volume of methanol and then air dried. Details are given in the table.

cpds	Reactants		Heating Time	Properties of Polymer
	m moles	$\frac{\text{moles esters}}{\text{moles glycol}}$		
Diester Carbowax 1500	1.732 3.203	0.54	6	Sol. H ₂ O, CHCl ₃ Gelatinous
Diester Polyglycol 600	2.666 2.962	0.90	5	Sticky oil
Diester Polyglycol 400	4.289 3.955	1.09	6	Sticky gum, forms thread
Diester Polyglycol 400	3.599 4.000	0.90	20	Viscous glue, no threads
Diester Me terephthalate Ethylene glycol	4.615 4.655 10.25	0.90	10	Low yield, reddish sticky gum
Diester Me sebacate Hexamethylene glycol	2.648 2.747 5.888	0.92	18	Greenish solid, tough and flexible

(3) Sodium dispersion (45% Na in toluene, courtesy of National Distillers) containing 3.42 gm (0.149 atoms) of Na, average particle size 20 μ , was suspended in 400 ml of dry tetrahydrofuran. Then 20 gm (0.0727 mole) of recrystallized dichloromethylanthracene were added in one portion at 3°C. The cooling bath was removed; after 2 hours of stirring the temperature had risen to 55°C and the solution was dark green. The mixture was then refluxed for 19 hours, cooled, and 5 ml of ethanol was added with no noticeable effect. Then 200 ml of water were added; the yellow suspension was filtered, and the precipitate (I) was washed with water. The filtrate had separated into two layers. Evaporation of the organic layer left solid (II) and the water layer contained 8.7 gm of solid, mostly NaCl.

Fraction I weighed 9.75 gm and was insoluble in common solvents. It contained a trace of chlorine, according to a sodium fusion, darkens at 245°C and shrivels, but does not melt up to 300°C. Fraction II melts to a red liquid at 175-185°C and is chlorine-free. A larger sample of I will be molded and tested.

(4) Disodiodihydroanthracene (A) was prepared in tetrahydrofuran as described previously. A 70% conversion of anthracene to (A) was assumed, based on the carbonation results.

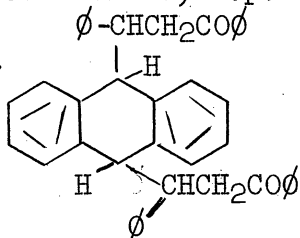
a. Ethylene oxide. To the (A) prepared from 7.99 gm (0.0448 mole) was added excess liquid ethylene oxide. The gummy product, 13.56 gm, obtained after hydrolysis and evaporation partially crystallized. Trituration with cold ether left 4.86 gm of colorless crystals, m.p. 113-116.5°C. A second crop from the filtrate contained 0.68 gm, m.p. 112-125°C. The oily residue, 5.58 gm, was dissolved in methanol-water-ethyl acetate and allowed to stand, giving ca. 1 gm needles, m.p. 275-279°C. The first crop was homogeneous, as shown by chromatography. Its infrared spectrum was similar to that of dihydroanthracene and also showed hydroxyl bands at 3.0 μ .

b. Propylene oxide. Details will be given in the next report. The procedure was similar to the above. Molecular distillation gave several solid or semisolid fractions.

c. Benzalacetophenone. To the (A) prepared from 5.17 gm (0.0291 mole) of anthracene was added dropwise at 0-5°C a solution of 9.04 gm (0.0435 mole) of benzalacetophenone in 65 ml of THF. After this amount had been added, the deep inky blue of the sodio compound changed abruptly to a pale green suspension. It was assumed that the yield (A) was 75%, since only three-fourths of the theoretical benzalacetophenone was used.

After stirring for 1-1/2 hours at 0°C the mixture was black. On addition of 5 ml of ethanol, the color changed abruptly to a suspension of colorless crystals, weighing 4.34 gm, m.p. 202-207.5°C, in a bright orange solution. When recrystallized from ethyl acetate-THF, there was obtained 0.28 gm, m.p. 265.5-267.5°C. The analytical sample was crystallized three times from dioxane, m.p. 268°C. A carbonyl band at 1670 cm⁻¹ was detected.

Anal. Calc. for



C, 88.56; H, 6.08.

Found: C, 86.42; H, 6.58

From the mother liquors was isolated 1.59 gm of anthracene, m.p. 212-216°C, and 1.72 gm of material melting at 190-204°C, by crystallization from dioxane-water.

The filtrate from the initial suspension was concentrated and it deposited 3.30 gm, m.p. 150-176°C. Recrystallization from EtOAc-MeOH-H₂O gave 2.15 gm, m.p. 166.0-168.5°C, as colorless needles. These on three crystallizations from benzene-petroleum ether melted at 206-207.5°C, but did not fluoresce.

Anal. Found: C, 86.47; H, 5.99

d. Ethyl haloacetates. In general, 2 moles of haloacetate per mole of anthracene were added at 0°C. After a short reaction time the only pure product isolated by hydrolysis was anthracene in a 10-25% recovery.

With longer reaction times or higher temperatures, some dihydroanthracene was obtained. The unaccounted-for starting material was mostly present as dark brown gums or oils, and chromatography on alumina did not locate any dihydrodiacetate.

e. Allyl chloride. Allyl chloride was added at 0-5°C to (A). A dramatic series of color changes was observed as the inky blue became a white suspension. After hydrolysis with saturated NH_4Cl the organic layer was vacuum distilled to remove the solvent, allyl chloride, and biallyl. Some anthracene has been recovered and work will be continued on this.

f. β -Propiolactone. The (A) was prepared from 6.41 gm of anthracene in 100 ml of THF. The chilled solution, under nitrogen, was treated dropwise in 40 minutes with a solution of 57.8 gm of β -propiolactone in 35 ml of THF. The color changed through green and tan to pale yellow. After an additional 1/2 hour of stirring at 0-5°C, the mixture was diluted with 50 ml of water. An odor of ethylene was detected. The aqueous layer was salted with NaCl and acidified with sulfuric acid, but only a small amount of gummy yellow material separated (ca. 0.5 gm) and this could not be induced to crystallize. It is probably a hydracrylate polymer of some sort.

Evaporation of the organic layer left 8.5 gm of a crude yellow solid, m.p. 95-102°C, which is probably mostly dihydroanthracene, since it is not acidic.

g. Benzoyl chloride. The (A) from 6.95 gm of anthracene was treated dropwise with a solution of 11.00 gm of benzoyl chloride in 30 ml of THF at 0°C for 1 hour. The color changed from inky blue through dark brown to a light brown heavy suspension. It was stirred at room temperature for 2 hours, then poured into a liter of ice water. A bright yellow paste oiled out of the solution and it did not crystallize overnight. After washing the paste with water, it was dissolved in benzene and diluted with petroleum ether. Cooling gave 3.43 gm of anthracene, m.p. 212-213°C. The mother liquors produced an oil on evaporation.

h. Acrylonitrile. The (A) from 6.47 gm of anthracene was treated dropwise with two equivalents of acrylonitrile in THF at 0-5°C in 1/2 hour. The red-brown mixture was stirred at room temperature for 14 hours. Addition of water gave a bright yellow solution which was saturated with salt, and the layers were separated. Evaporation of the organic layer gave a solid, most of which dissolved in hot dioxane. Addition of water precipitated 3.56 gm of dihydroanthracene, m.p. 103-106°C; the identity was checked by infrared spectrum and trinitrobenzene complex. The dioxane-insoluble material weighed 0.78 gm, m.p. 190-230°C dec.

In another experiment ca. 0.1 gm, m.p. 230-255°C dec was obtained from 5.11 gm of anthracene. Its infrared spectrum showed absorption at 1670 cm^{-1} , which may be due to conjugated carbonyl. There was also recovered 2.43 gm of dihydroanthracene, m.p. 105-109°C.

Reformatsky Reaction

(5) A mixture of 100 ml of THF, 6.24 gm of anthraquinone, and 13.5 gm of ethyl iodoacetate was stirred at 50°C while 4.57 gm of activated zinc was added. On heating to reflux, reaction set in and the solution turned bright green; after 20 minutes, the color was olive. After an additional 20 minutes of reflux, 50 ml of 20% HCl were added to the cooled solution. The layers were separated and 0.17 gm of solid anthraquinone, m.p. 265-271°C, was filtered off. The water layer was extracted with ether; the combined organic layers were water washed, dried with MgSO₄, and evaporated on the water pump. The dark brown oil, 10.49 gm, resisted attempts to crystallize it, so it was chromatographed on alumina. One liter of petroleum ether (60-75°C) eluted 1.18 gm of tan solid, which softened at 68-72°C and melted at 116-125°C; 300 ml of 10% benzene in petroleum ether and 200 ml of 10% ether in petroleum ether eluted 1.07 gm of a pale yellow solid, m.p. 79.5-81.5°C, which was twice crystallized from isooctane as needles, m.p. 79.5-80.5°C. Analysis is pending.

Further elution with more polar eluents gave dark oils. The total recovery from the column was 8.04 gm.

