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CONJUGATED POLYMER SYSTEMS
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FINAL REPORT

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Summary

Studies by Gerald Staffin of the polymerization of 4-bromo-2,6-dimethylphenol to poly-(2,6-dimethyl-p-phenylene oxide), presented in earlier progress reports, have been summarized in a doctoral dissertation and a paper scheduled for publication in the Journal of the American Chemical Society in 1960.

Extension of these studies by Dr. C. J. Kurian to dialkyl o- and p-bromophenols in which the two alkyl groups were various combinations of methyl, allyl, propyl and phenyl indicated that all of these compounds were readily polymerizable. In general, the o-bromophenols gave lower yields and lower molecular weights.

The allyl phenol polymers became insoluble and infusible after exposure to the atmosphere for a few days, evidently due to crosslinking through the allyl double bonds.

Polymer made by oxidative polymerization of 2,6-dimethylphenol according to A. S. Hay, H. S. Blanchard, G. F. Endress and J. W. Eustance, J. Am. Chem. Soc., **81**, 6335 (1959) had infrared and ultraviolet spectra essentially identical to the poly(2,6-dimethyl-p-phenylene oxide) prepared from the 4-bromo monomer. This indicates that the majority of the units in the oxidative polymer are indeed p-linked.

The oxidative polymerization gave polymer of considerably lower molecular weight from 2,6-diallylphenol and failed entirely for 2,6-dibromophenol, indicating more critical structural requirements for satisfactory polymerization by this procedure, as compared to the bromine displacement procedure.

Investigation of the mechanism of these interesting and potentially useful polymerization procedures is continuing under other auspices.

Experimental

Preparation of 2-Methylphenyl Allyl Ether

o-Cresol = 25.0 g.
Allyl Bromide = 28.0 g.
K_2CO_3 (anhydrous) = 38.5 g.
Acetone = 33.5 g.

The above reagents were mixed and heated under reflux for six hours. The allyl ether formed was extracted and fractionally distilled. The fraction which distilled over between 98-100° (17 mm.) was collected. This fraction weighed 21.0 g.

Claisen Rearrangement of 2-Methylphenyl Allyl Ether

Wt. of the ether = 19.5 g.
N,N-diethylaniline = 10.0 g.

The above reagents were mixed and heated under reflux in a current of nitrogen at 230-240° for one hour. The 2-methyl-6-allyl phenol formed was extracted and purified by fractional distillation. The major fraction distilled over between 115-116° (17.5 mm.) and it weighed 13.5 g. This was redistilled and the fraction which boiled at 114° (16.5 mm.) was collected and used in the polymerization studies.

Preparation of 4-Phenylphenyl Allyl Ether

4-Hydroxy biphenyl = 40 g.
Allyl bromide = 28.5 g.
K_2CO_3 = 39 g.
Acetone = 35 cc.

The above reagents were mixed in a 1-liter round-bottomed flask fitted with a water condenser and heated under reflux for four and a half hours. The yield of 4-phenylphenyl allyl ether was 41 g.

Claisen Rearrangement of the Allyl Ether

4-Phenylphenyl allyl ether = 38 g.
N,N-diethylaniline = 20 g.

The reagents were mixed and heated in a flask fitted with a nitrogen inlet tube and a condenser. The temperature was slowly raised to 230-240° and maintained at that temperature for about fifty minutes. A steady stream of nitrogen was maintained throughout the course of heating.

The 2-allyl-4-phenyl phenol was purified by extraction and fractional distillation and the fraction which boiled at 126° (0.2 mm.) was collected; yield, 30 g., m.p. 73-74°.

Preparation of Phenyl Allyl Ether

Wt. of the phenol = 120 g.
Allyl bromide = 155 g.
K_2CO_3 (anhydrous) = 211.2 g.
Acetone = 75 cc.

The above reagents were mixed and heated under reflux for four and a half hours. The allyl ether formed was purified by extraction and fractional distillation. The fraction which boiled at 90° (25.0 mm.) was collected. It weighed 130.0 g. The fraction which distilled at a higher temperature (last fraction) weighed 25.5 g.

Claisen Rearrangement of Allyl Phenyl Ether

Wt. of the ether = 125 g.
N,N-diethyl aniline = 65 g.

The above mixture was heated in an oil bath for three hours in a current of nitrogen at 235°. (Note: The temperature of the oil bath was raised to 230° in the course of thirty to forty-five minutes.)

The 2-allylphenol formed was extracted and purified by distillation. The fraction which distilled over between 107-110° (21 mm.) was collected. This was redistilled and the fraction which boiled at 108° (19 mm.) was collected; yield of 2-allylphenol = 52 g.

Preparation of 2-Allylphenyl Allyl Ether

2-Allylphenol = 44 g.
Allyl bromide = 40 g.
K_2CO_3 (anhydrous) = 55.5 g.
Acetone = 48 cc.

The above reagents were mixed in a one-liter round-bottomed flask fitted with a water condenser and heated under reflux for four and a half hours. The fraction which distilled over between 78-80° (1.25 mm.) was collected; yield of 2-allylphenyl allyl ether = 51.0 g.

Claisen Rearrangement of 2-Allylphenyl Allyl Ether

2-Allylphenyl allyl ether = 49.5 g.
N,N-diethyl aniline = 25.0 g.

The above reagents were mixed in a two-necked round-bottomed flask fitted with a nitrogen inlet tube and a condenser. It was then heated in an oil bath. The bath temperature was raised to 230° gradually and the heating was continued for about an hour, keeping the bath temperature between 230-240°.

The 2,6-diallylphenol formed was purified by extraction and fractional distillation. The fraction which boiled at 78-80° (0.8 mm.) was collected. This was redistilled and the fraction which distilled at 79° (0.8 mm.) was collected; yield of 2,6-diallylphenol = 25.0 g.

Preparation of 4-methylphenyl allyl ether

p- cresol = 45 g.
Allyl bromide = 51 g.
K_2CO_3 (anhydrous) = 69.5 g.
Acetone = 60 cc.

The procedure for the allyl ether formation and extraction were the same as described above.

4-Methylphenyl allyl ether was purified by fractional distillation and the fraction which boiled at 100° (16 mm.) was collected; the yield of the product = 51 g.

Claisen rearrangement of the allyl ether

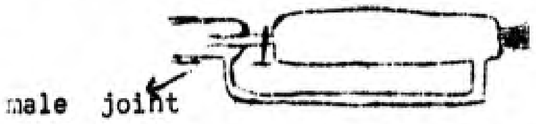
A mixture of 51 g. of 4-methylphenyl allyl ether with 26 g. of N,N-diethyl aniline was heated in an oil bath in a stream of nitrogen. The temperature of the bath was slowly raised to 230°. It was maintained at that temperature for two and one-half hours.

The yield of 2-allyl-4-methyl phenol was 32 g., b.p. 119-120° (15.5 mm.).

General method of polymerization

Ref:- A. S. Hay et al., J. A. C. S., 81,6335, (1959).

A known amount of cuprous chloride (1/20 equivalent) is weighed out into a two necked flask. Nitrobenzene and pyridine are then added to the flask. The flask is connected to an oxygen burette through one neck and on to the other one is fitted a dropping funnel of the type shown below:



The desired amount of phenol (1 equivalent) dissolved in nitrobenzene is added to the dropping funnel. The whole system is then evacuated by connecting it to an aspirator. The system is then filled with oxygen at atmospheric pressure and shaken for about five minutes by which time the copper goes into solution and is oxidized to the cupric state. Then the phenol solution is added to the reaction flask (from the dropping funnel) and the shaking is continued until there is no more absorption of oxygen. When no more oxygen is absorbed the shaking is stopped and the content of the reaction flask is poured into excess methanol containing 5%, by volume, of concentrated hydrochloric acid which is kept stirred, and the precipitated material (if any) is redissolved in chloroform and reprecipitated. The process is repeated twice more to purify the polymer. The polymer is then filtered, dried and weighed.

Polymerization of Phenol

The phenol was purified by fractional distillation under reduced pressure just before use. The fraction which distilled over/126° (123.0 mm.) was collected and used in the study.

Experiment G-H-1

Wt. of Phenol = 2.01g. (in 10 cc nitrobenzene)
Wt. of CuCl = 0.08g.
Nitrobenzene = 60 cc
Pyridine = 20 cc

The procedure for polymerization was the same as described under general method of polymerization. Oxygen absorption became noticeable in about 15 minutes and about 75 cc. of oxygen (room temperature) was absorbed in about four hours. The shaking was continued for two days and the total amount of oxygen absorbed was 85 cc. (room temperature and atmospheric pressure).

The contents of the flask were then poured into about 300 cc. of methanol (containing concentrated hydrochloric acid, 5% by volume). No precipitation was observed, so water (about 20-30 cc) was added to the above solution dropwise with stirring. Some cloudiness appeared. The stirring was stopped and after a few hours some oil settled down at the bottom. This was separated from the top layer of liquid in a separating funnel and was washed with water once (to remove any cupric salt that might have gone into the oily layer). It was then distilled under reduced pressure when all the nitrobenzene distilled over. The residue left in the pot could not be distilled over under the pressure used (0.3 mm.). It weighed about 0.6 g. It is a dark, very viscous oil.

Polymerization of 2,6-Dibromophenol

Experiment G-H-2

2,6-Dibromophenol (Eastman) was distilled just before use. The fraction which distilled at 106° (2.9 mm.) was used in the polymerization study.

Weight of 2,6-dibromophenol = 2.05 g. (in 10 cc nitrobenzene)
CuCl = 0.08 g.
nitrobenzene = 60 cc.
pyridine = 20 cc.

The polymerization procedure was the same as described in the general method. Even after shaking for one and one-half days in oxygen there was no absorption of oxygen, probably indicating that it does not undergo polymerization by this method.

Polymerization of 2,6-dimethylphenol

2,6-Dimethyl phenol (Eastman) was used without any further purification.

Experiment G-H-3

2,6-dimethyl phenol = 0.97 g. (in 10 cc. nitrobenzene)

CuCl = 0.04 g.

Nitrobenzene = 30 cc.

pyridine = 9 cc.

Procedure was the same as described in the general method. The oxygen absorption was practically complete in about thirty minutes. Total oxygen absorbed is approximately 300 cc. The contents of the reaction flask were then poured into 300 cc. of methanol containing concentrated HCl (5% by volume) which was kept stirred. The precipitated polymer was taken up in $CHCl_3$ and reprecipitated by acidic methanol (5% of concentrated HCl by volume) and this process was repeated once more. The polymer was filtered, dried and weighed; yield of polymer = 0.87 g.

Softening point

At 250° it begins to show some slight change in color. By 300° it is slightly brown; it does not soften to a viscous mass, but becomes pliable at that temperature (300°).

Viscosity of G-H-3

Nsp	0.5811	0.4056	0.3107
Conc.	0.4743	0.3689	0.3018
Nsp/c	1.225	1.099	1.029

$$(n) = 0.8$$

Experiment G-H-3A

In another experiment 2,6-dimethylphenol (1.954 g.) dissolved in nitrobenzene (60 cc.) and pyridine (18 cc.) was stirred with 0.08 of CuCl in an atmosphere of nitrogen. After about one and one-half hours the stirring was stopped, and the contents poured into acidic methanol when the polymer precipitated. The polymer was purified as in the previous experiment. It weighed 1.7 g. and its softening point was the same as that for sample G-H-3.

Polymerization of 2-methyl-6-allylphenol

Experiment G-H-4

2-methyl-6-allyl-phenol = 2.02 (in 10cc. nitrobenzene)
CuCl = 0.08
Nitrobenzene = 60 cc.
Pyridine = 20 cc.

The polymerization procedure was the same as described in the general method. The shaking was stopped after one day. It absorbed about 250 cc. of oxygen. The contents were poured into 300 cc. of methanol containing concentrated HCl (5% by volume), but there was no observable precipation. However, with an addition of water (about 20-30 cc.) some oil separated out. This was separated in a separatory funnel, washed with water and distilled under reduced pressure. The nitrobenzene distilled over and the residue left behind weighed 2 g.. In appearance it is a viscous dark brown oil, evidently polymer of low molecular weight.

Polymerization of 2-allylphenol

Experiment G-H-5

2-allylphenol = 2.01 g. (in 10 cc. nitrobenzene)
CuCl = 0.08 g.
Nitrobenzene = 60 cc.
Pyridine = 18 cc.

Total time of shaking = two and one-half days.

The contents of the reaction flask were poured into 300 cc. of methanol containing concentrated hydrochloric acid (5% by volume) which was kept stirred. No precipitation was absorbed. Addition of water (20-30 cc.) produced some cloudiness. The oil that settled to the bottom of the flask, on standing, was separated, washed with water, and then distilled under reduced pressure. All the nitrobenzene distilled over and the residue left behind weighed 1.0 g. In appearance it was a dark very viscous oil.

Polymerization of 2,6-diallylphenol

Experiment G-H-6

2,6-diallylphenol = 2.07 g. (in 10 cc. nitrobenzene)
CuCl = 0.08 g.
Nitrobenzene = 60 cc.
Pyridine = 20 cc.

About 200 cc. of oxygen was taken up in the first forty-five minutes. From then on absorption of oxygen was slow. Total time of shaking was twenty-seven hours. Total oxygen absorbed was about 240 cc.

In this case also no solid polymers separated out on addition of the above solution to acidic methanol. However, on addition of water-dropwise- a dark viscous oil separated out. This was washed with water and distilled. Nitrobenzene distilled over. The residue left behind was 2.0 g. of dark very viscous oil.

Polymerization of 2-allyl-4-methylphenol

Experiment G-H-7

2-allyl-4-methylphenol = 2 g. (in 10 cc. nitrobenzene)
CuCl = 0.0669
Nitrobenzene = 60 cc.
Pyridine = 18 cc.

Initially about 20 cc. of oxygen was absorbed but there was no further absorption even after one day. Adding the contents of the flask to methanol containing hydrochloric acid (95.5 by volume) gave no precipitation. Then water was added dropwise. A cloudiness appeared, and an oil separated. This oily layer was washed with water and then distilled. Nitrobenzene distilled over. The residue left behind was 1.2 g. of dark viscous oil.

Polymerization of 2-allyl-4-phenylphenol

Experiment G-H-8

2-allyl-4-phenylphenol = 2 g. (in 10 cc. nitrobenzene)
CuCl = 0.08 g.
Nitrobenzene = 60 cc.
Pyridine = 20 cc.

After shaking for one and one-half days, the reaction was poured into 300 cc. of methanol containing concentrated hydrochloric acid (5% by volume). There was no precipitation. On addition of water an oily layer separated out. It was washed with water and then distilled under reduced pressure. All the nitrobenzene distilled over leaving a dark viscous residue which weighed 1.7 g.

Polymerization 2,4-dimethylphenol

Experiment G-H-9

2,4-dimethylphenol (Eastman) was distilled just before use. The fraction which boiled at 96° (12 mm.) was collected and used in the polymerization study.

2,4-dimethylphenol = 2.1 g. (in 10 cc. of nitrobenzene)
CuCl = 0.08
Nitrobenzene = 60 cc.
Pyridine = 20 cc.

On shaking for one day, 225 cc. of oxygen was absorbed. There was no precipitation on pouring into the methanol containing hydrochloric acid. Addition of water caused a cloudiness and an oil separated. This layer was washed with water and distilled under reduced pressure. Nitrobenzene distilled over leaving behind a dark viscous oily substance weighing 1.5 g.

Preparation of 2-methyl-4-bromophenol

o-Cresol = 75 g.
$CHCl_3$ = 310 cc.
Bromine = 111 g.

o-Cresol (75 g.) was dissolved in 250 cc. of chloroform. Bromine (114 g.) dissolved in 60 cc. of chloroform was added slowly to the phenol solution which was kept stirred. When most of the bromine was added the reaction flask was slightly warmed and the addition of bromine was completed. When no further evolution of hydrogenbromide was observed, the stirring was stopped. The chloroform was distilled off and the 2-methyl-4-bromophenol was purified by fractional distillation under vacuum.

The first fraction, collected between 70° and 80° (1.3 mm.), weighed 36.5 g. (28.1%).

The second fraction-which was the major fraction distilled at 81° (1.0mm.). This weighed 91 g. (70%).

Preparation of 2-methyl-4-bromophenyl allyl ether

2-methyl-4-bromophenol = 91g.
K_2CO_3 (anhydrous) = 80.7 g.
Allyl bromide = 58.9 g.
Acetone = 73.4 g.

The above reagents were mixed in a one litre flask and heated under reflux for four hours. The flask was then allowed to cool. Water (400 cc.) was added to the flask. The contents were then extracted with ether (650 cc.). The ether extract was washed with 10% sodiumhydroxide solution three - four times (500 cc. of 10% sodiumhydroxide was used). It was then washed with distilled water and dried over anhydrous potassium carbonate overnight.

The ether extract was then filtered and the ether distilled off at atmospheric pressure. The remaining liquid was fractionally distilled.

The middle fraction - which was the major portion - distilled at 87° (1.0 mm.). This weighed 73 g. (66%). A higher boiling fraction was also obtained (probably due to C-alkylation). Boiling point of this fraction was 90 - 102° (1 mm.) and it weighed 16 g. (14.5%).

The middle fraction was further purified by recrystallization from petroleum ether at low temperature. The white crystals were taken up in anhydrous ether and dried over anhydrous sodium sulfate overnight. The ether was then distilled and the remaining liquid was fractionally distilled. The fraction which distilled at 88° (1.1 mm.) was collected.

$n^{26.5}D = 15534$

Analysis calculated for $C_{10}H_{11}OBr$: C,52.86; H, 4.85; Br, 35.24

Found: C, 52.60; H, 5.00; Br, 35.46

Claisen rearrangement of 2-methyl-4-bromophenyl allyl ether

2-Methyl-4-bromophenyl allyl ether = 57 g.
N,N-Diethylaniline = 30 g.

2-Methyl-4-bromophenyl allyl ether (57 g.) was dissolved in N,N-diethylaniline (30 g.) and was heated in a stream of nitrogen at 235° for about one hour. The heating was then stopped and contents of the flask were allowed to cool in a nitrogen atmosphere.

When cooled the contents were extracted with petroleum ether (500 cc.) The extract was washed three-four times with ice-cooled dilute sulfuric acid (50 cc. of concentrated sulfuric acid in 600 cc. of water), followed by cooled distilled water.

The phenol was then extracted from the petroleum ether solution by washing with Claisen alkali about four times (Claisen alkali - 70 g. of potassium hydroxide was dissolved in 50 cc. water, cooled, and then 200 cc. methanol was added and cooled again before use in the extraction).

The alkali extract was then acidifiedwith dilute hydrogen chloride. (During this process the alkcli solution was kept cooled in ice. The dilute hydrogen chloride used also was cooled by adding ice to it.)

The precipitated phenol was extracted with ether, The ether extract was washed with water, and then dried over anhydrous sodium sulphate overnight.

The ether was then distilled. The remaining liquid was fractionally distilled. The first fraction, which boiled below 112° (2mm.), weighed 6 g. (10.5%).The second fraction collected was that which distilled between 112°-113°C (2 mm.). This fraction weighed 30 g. (52.6%).

It was further purified by recrystallization from petroleum ether at low temperature. The recrystallized product was dissolved in ether, dried over sodiumbisulfite and fractionally distilled. The fraction which boiled at 101° (1.2mm.) was collected and used in the polymerization experiments; n^{33}_D 1.5695

Analysis calculated for $C_{10}H_{11}OBr$: C,52.86; H, 4.85; Br, 35.24

Found: C, 52.66; H, 4.96; Br, 35.34

NOTE: When the Claisen rearrangement was carried out in absence of any added solvent (like N,N-Diethylaniline) there was considerable decomposition and a mixture of products were obtained. This mixture could not be purified by fractional distillation.

Reduction of 2,6-Diallylphenol

2,6-Diallylphenol = 16.5 g.
Weight of catalyst (5% Pd on C) = 1.6 g.
Benzene = 100 cc.

To the solution of 2,6-diallylphenol in benzene was added the catalyst. (The quantities of substances taken are given above). The hydrogenation was carried out in a medium pressure hydrogenation apparatus. The initial pressure of hydrogen was 51 p.s.i.. It dropped to 34.5 p.s.i. in about 15 minutes. There was no further drop in pressure on continued shaking. The contents of the reaction flask were then filtered to remove the catalyst and the filtrate was distilled under vacuum after removing all the benzene - by distillation at atmospheric pressure - The fraction which distilled over between 69° and 70° (0.4 mm.) was collected; yield of 2,6-dipropylphenol= 14 g.

Bromination of 2,6-dipropylphenol

2,6-Diprophlphenol	= 13.8 g.
$CHCl_3$	= 110 cc.
Bromine	= 12.5 g.

In a three-necked round-bottomed flask fitted with a stirrer, a dropping funnel and a condenser was taken 2,6-diprophyphenol (13.8 g.) in 90 cc. of chloroform. The solution was kept stirred. To this was added a solution of 12.5 g. of bromine in 20 cc. of chloroform dropwise. Towards the end of the reaction the flask was slightly warmed to drive off any dissolved hydrogen bromide and thus to facilitate the completion of the reaction. The flask was then cooled and four-five g. of sodium-bisulfite was added to destroy excess of bromine present in the system. The chloroform was repeatedly washed with water until the water layer was colorless. It was found that after three or four washings with water the chloroform layer was found to take up a yellow color which slowly disappeared on standing. The chloroform layer was dried over sodiumbisulfate (anhydrous) and distilled. The fraction which boiled at 107° (0.5 mm.) was collected. It weighed 11.5 g. It was further purified by low temperature recrystallization from petroleum ether (boiling point 30°-60°). The recrystallized material was redissolved in petroleum ether, dried over sodium besulfate and fractionally distilled twice before use in polymerization. The fraction which boiled at 107.5° (0.6 mm.) was collected and used for the polymerization experiments.

Potassium ferricyanide initiated polymerization (in an inert atmosphere).

Experiment NP-2

2-Methyl-4-bromo-6-allylphenol (3.353 g.) in benzene (25 cc.) was added to a three-necked, round bottomed flask fitted with a stirrer, a gas inlet tube, a dropping funnel and a gas outlet. To this was added benzene (250 cc.) water (100 cc.) and potassium hydroxide (1.0 g.). Purified nitrogen was passed through the system for about two hours. A solution of potassium ferricyanide (0.4868 g.) in water (30 cc.) was then added dropwise through the dropping funnel with continual stirring. The stirring was continued for one and one-half days. Throughout the experiment nitrogen was bubbled through the reaction mixture.

After one and one-half days of stirring the reaction was stopped by adding dilute nitric acid (150 cc; approximately 1.0N) The contents were poured into a separatory funnel, washed with dilute nitric acid, then with distilled water. The benzene layer was then concentrated by evaporation in a roto-vap to about 50 or 60 cc. Then it was filtered and freeze-dried. The polymer formed was then purified by redissolving it in benzene and adding to excess methanol which was kept stirred. The precipitated polymer was again taken up in benzene and freeze-dried; weight of the polymer obtained = 1.388 g. (67.2%)

Experiment NP-9

Polymerization of 2-allyl-4-bromo-6-phenylphenol

The experimental conditions of polymerization were the same as described in Experiment NP-2. The quantities of reagents used are given below;

Weight of 2-Allyl-4-bromo-6-phenylphenol	= 1.893 g.
Weight of Potassium hydroxide	= 0.5 g.

Experiment NP-9 (cont.)

Weight of Potassium ferricyanide = 0.2155 g. (in 30 cc. water)
Volume of Water = 100 cc.
Volume of Benzene = 275 cc.
Time of Reaction = one and one-half days

Weight of Polymer formed = 0.242 g. (17.8 %)

Experiment NP-12

Polymerization of 2-propyl-4-bromo-6-phenylphenol.

Polymerization procedure and extraction and purification of the polymers were similar to that in Experiment NP-2 and Experiment NP-9. The quantities of the reagents used are given below:

2-Propyl-4-bromo-6-phenylphenol = 3.503 g.
Volume of Benzene = 275 cc.
Volume of Water = 100 cc.
Weight of Potassium Hydroxide = 0.7 g.
Weight of Potassium ferricyanide = 0.3960 g. (in 30 cc. water)
Time of reaction = 1.5 days

Weight of the polymer formed = 0.484 g. (19.2%)

Phenol	Phenol:Cat.	Time of Reaction	Percentage conversion to polymer	[n]
2-Methyl-4-bromo-6-allyl	10:0.1	1.5 days	67.2%	0.168
2-Methyl-4-bromo-6-propyl	"	"	65.7	0.144
2-Allyl-4-bromo-6-phenyl	"	"	17.8	0.108
2-Propyl-4-bromo-6-phenyl	"	"	19.2	0.100

VISCOSITY DATA

Experiment No. NP-2

Conc.	0.8820	0.6300	0.4900	0.4009
n_{sp}	0.1733	0.1191	0.0902	0.0720
n_{sp}/c	0.1965	0.1891	0.1841	0.1796

(n) = 0.168

Experiment No. NP-9

Conc.	0.7840	0.5600	0.4356	0.3564
n_{sp}	0.0880	0.0622	0.0489	0.0391
n_{sp}/c	0.1122	0.1110	0.1122	0.1097

(n) = 0.108

Experiment No. NP-12

Conc.	0.8140	0.5814	0.4522
n_{sp}	0.08889	0.0613	0.0476
n_{sp}/c	0.1092	0.1055	0.1051

(n) = 0.100

Experiment Gd-4

Polymerization of 2-allyl-4-methyl-6-bromo phenol

Polymerization procedure and extraction and purification of the polymer were similar to that in Experiment NP-2. The quantities of the reagents used are given below.

2-allyl-4-methyl-6-bromophenol = 4.411 g.
Volume of Benzene = 290 cc.
Water = 100 cc.
Potassium Hydroxide = 1.2
Potassium Ferricyanide = 0.6398 (in 30 cc. water)
Time of reaction = one and one-half days
Weight of the polymer formed = 0.515 g.

Experiment Gd-1

Polymerization of 2-allyl-4-phenyl-6-bromophenol

For experimental procedure see Experiment NP-2

2-allyl-4-phenyl-6-bromophenol = 4.293 g.
Potassium Ferricyanide =0.439 g. (in 30 cc. water)
Benzene = 280 cc.
Water = 100 cc.
Potassium Hydroxide = 0.95 g.
Time of Reaction = one and one-half days
Weight of the polymer formed = 0.1346 g.

Experiment Gd-12

Polymerization of 2,6-diallyl-4-bromophenol

For experimental procedure see Experiment NP-2

2,6-diallyl-4-bromophenol = 3.227 g.

Benzene = 275 cc.

Water = 100 cc.

Potassium Hydroxide = 0.8 g.

Potassium Ferricyanide = 0.42 g. (in 30 cc. water)

Time of reaction = one and one-half days

Weight of the polymer formed = 0.7 g.

Experiment Gd-16

Polymerization of 2,6-dipropyl-4-bromophenol

For experimental procedure see Experiment NP-2

2,6-dipropyl-4-bromophenol = 2.23 g.

Volume of Benzene = 275 cc.

Volume of Water = 100 cc.

Potassium Ferricyanide = 0.2857 g. (in 30 cc. water)

Potassium Hydroxide = 0.6 g.

Time of reaction = one and one-half days

Weight of Polymer formed = 0.42 g.

Experiment Gd-17

Polymerization of 2,6-dipropyl-4-bromophenol

2,6-dipropyl-4-bromophenol = 2.23 g.
Volume of Benzene = 275 cc.
Volume of Water = 100 cc.
Potassium Ferricyanide = 0.1429 g. (in 30 cc. water)
Potassium Hydroxide = 0.6 g.
Time of reaction = one and one-half days
Weight of polymer formed = 0.21 g.

Experiment Gd-7

Polymerization of 2,Propyl-4-methyl-6-bromophenol

Exp. procedure same as in Experiment NP-2

2-Propyl-4-methyl-6-bromophenol = 3.867 g.
Volume of Benzene = 295 cc.
Volume of Water = 100 cc.
Potassium Ferricyanide = 0.1438 (in 30 cc. water)
Potassium Hydroxide = 1.04 g.
Time of reaction = one and one-half days
Weight of the polymer formed = 0.06 g.

Experiment Gd-9

Polymerization of 2-propyl-4-phenyl-6-bromophenol

Experimental procedure same as in Experiment NP-2

2-propyl-4-phenyl-6-bromophenol = 4.95 g.

Benzene = 295 cc.

Water = 100 cc.

Potassium Ferricyanide = 0.56 g. (in 30 cc. water)

Potassium Hydroxide = 1.05 g.

Time of reaction = one and one-half days

Weight of polymer formed = 1.14 g.

VISCOSITY DATA

Experiment Gd-4

Conc.	0.9100	0.7078	0.5791	
n_{sp}	0.0377	0.0273	0.0186	(n) = 0.032
n_{sp}/c	0.0414	0.0386	0.0321	

Experiment Gd-12

Conc.	0.8071	0.6278	0.5136	
n_{sp}	0.1232	0.0944	0.0771	(n) = 0.147
n_{sp}/c	0.1526	0.1504	0.1501	

Experiment Gd-16

Conc.	0.9500	0.7389	0.6045	
n_{sp}	0.1161	0.0900	0.0700	(n) = 0.111
n_{sp}/c	0.1222	0.1218	0.1158	

Experiment Gd-17

Conc.	1.5186	1.1811	0.9664	
n_{sp}	0.1715	0.1312	0.1059	(n) = 0.104
n_{sp}/c	0.1129	0.1111	0.1096	

Experiment Gd-9

Conc.	0.6900	0.5367	0.4391	
n_{sp}	0.0151	0.0115	0.0089	(n)=0.019
n_{sp}/c	0.0219	0.0214	0.0203	

Softening Points of the Polymers

Gd-4	62-70°C
Gd-12	75-85°C
Gd-16	142-155°C
Gd-17	88-95°C
Gd-7	60-65°C
Gd-9	55-62°C

General Polymerization Procedure Using Lead Dioxide Catalyst

The procedure in general is the same as in Experiment NP-2 except that lead dioxide is added to reaction mixture in place of potassium ferricyanide solution.

Experiment Gd-6

Polymerization of 2-allyl-4-methyl-6-bromophenol

Weight of the Phinol =4.411 g.

Weight of Lead Dioxide = 0.2324 g.

Benzene =290 cc.

Water = 100 cc.

Potassium Hydroxide = 1.2 g.

Time of reaction = one and one-half days

Weight of polymer formed = 0.04 g.

Experiment Gd-3

Polymerization of 2-allyl-4-phenyl-6-bromophenol

Weight of the phenol = 4.293 g.

Volume of Benzene = 280 cc.

Lead Dioxide = 0.1776

Potassium Hydroxide = 1.0 g.

Water = 100 cc.

Time of reaction = one and one-half day

Weight of polymer formed = 0.44 g.

Experiment Gd-8

Polymerization of 2-propyl-4-methyl-6-bromophenol

Weight of the phenol = 3.867 g.

Volume of Benzene = 295 cc.

Water = 100 cc.

Potassium hydroxide = 1.04 g.

Lead Dioxide = 0.2015

Time of reaction = one and one-half days

Weight of polymer formed = 0.02 g.

Experiment Gd-10

Polymerization of 2-propyl-4-phenyl-6-bromophenol

Weight of the phenol = 4.95 g.

Volume of Benzene = 295 cc.

Water = 100 cc.

Potassium hydroxide = 1.05

Lead dioxide = 0.2035 g.

Time of reaction = one and one-half days

Weight of the polymer formed = 0.32 g.

Experiment Gd-14

Polymerization of 2,6-diallyl -4-bromophenol

Weight of the phenol = 3.227 g.

Volume of Benzene = 275 cc.

Water = 100 cc

Lead dioxide = 0.1525 g.

Potassium hydroxide = 0.8 g.

Time of reaction = one and one-half days

Weight of the polymer formed = 1.205 g.

Experiment Gd-18

Polymerization of 2,6-dipropyl-4-bromophenol

Weight of the phenol = 2.23 g.

Volume of Benzene = 275 cc.

Water = 100 cc.

Lead Dioxide = 0.1038 g.

Potassium hydroxide = 0.6 g.

Time of reaction = one and one-half days

Weight of the polymer formed = 0.81 g.

VISCOSITY DATA

Gd-3

Conc.	0.8114	0.6311	0.5164	
n_{sp}	0.0226	0.0180	0.0158	$(n)=0.034$
n_{sp}/c	0.0279	0.0285	0.0306	

Gd-10

Conc.	1.0357	0.8056	0.6591	
n_{sp}	0.0266	0.0195	0.0164	$(n)=0.022$
n_{sp}/c	0.0257	0.0242	0.0249	

Gd-14

Conc.	0.8014	0.6233	0.5100	
n_{sp}	0.0767	0.0598	0.0492	$(n)=0.098$
n_{sp}/c	0.0957	0.0959	0.0965	

Gd-18

Conc.	1.058	0.7557	0.5878	
n_{sp}	0.1117	0.0785	0.0587	$(n)=0.096$
n_{sp}/c	0.1056	0.1039	0.0999	

SOFTENING POINT OF THE POLYMERS

Gd-3	75-85°C
Gd-10	70-80°C
Gd-14	50-54°C
Gd-18	135-140°C