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Determination of Some Color Components Present in Petroleum Resin

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ABSTRACT

In a previous report, it was found that some of the color components in the starting material of petroleum resin were cyclopentadiene, methylcyclopentadiene, and their dimers. In the present study, other color components than those mentioned above and the cause of coloring petroleum resin by cyclopentadiene and methyl derivative were investigated. Norbornadiene and ethylidene norbornene were found also to be color components, and the structures of some conjugated systems which color the petroleum resin were inferred from the data of ESR spectra.

INTRODUCTION

The color of industrially produced petroleum resin is ordinarily dark yellow to red, which is in the rank of 10 to 12 G as measured by the Gardner scale. It was reported in a previous paper that the starting material of the resin reacted with maleic anhydride to remove some color components from it. The reaction of starting material with maleic anhydride involves both Diels-Alder reaction [1, 2] and copolymerization [3]. The former consists of maleic anhydride with cyclopentadiene and methylcyclopentadiene, and the latter, maleic anhydride with olefinic compounds. The product containing other color components from copolymerization was further investigated. The cause of coloring of polystyrene by cyclopentadiene derivatives in the polymerization of styrene and cyclopentadiene derivatives as a model system was also examined by using ESR spectra.

RESULTS AND DISCUSSION

A constant amount of the starting material of petroleum resin was reacted with different amount of maleic anhydride, followed by vacuum distillation to obtain refined fractions, and by cationic polymerization to afford a lighter resin. Table 1 shows the correlation between the amount of product copolymerized by the reaction of the starting material with different amounts of maleic anhydride and the color rank of petroleum resin. As is shown by the data, the amount of product copolymerized increases with a decrease in color rank (lighter color) of the petroleum resin. Other color components might be contained in the copolymer. Of course, since the copolymerization proceeds through a thermal free-radical mechanism because of the different amounts of the copolymerized products between under air and nitrogen atmospheres, the copolymerization [4] of cyclopentadiene and methylcyclopentadiene with maleic anhydride may take place in the presence of a free-radical species to involve cyclopentadiene and methylcyclopentadiene in the copolymer, and as a result, the color of the resin becomes lighter. But from the data that at a concentration of maleic anhydride as low as 1 wt % (0.01 $\underline{M}$) versus the starting material, the Diels-Alder reaction rather than the copolymerization takes place. Cyclopentadiene and methylcyclopentadiene as well as their Diels-Alder adducts [5] do not copolymerize with maleic anhydride. Thus the fact that the more the amount of the copolymerized product is, the lighter the color of the petroleum resin becomes, indicates with certainty that other color components besides cyclopentadiene and methylcyclopentadiene removed by the Diels-Alder reaction are involved in the copolymer. Some components that are likely to color petroleum resins among the changed components between the starting material and the refined fractions obtained from vacuum distillation of the reaction mixture of the starting material with maleic anhydride were investigated by use of GLPC. Further, from the data obtained by pyrolysis of the copolymer as described in a previous paper, styrene and its derivatives, and indene and its derivatives that are main components in the starting material are, of course, involved in the copolymer, but any homopolymer from each of those does not become colored. In addition to

TABLE 1. Correlation between the Amount of Copolymerized Product and the Color Rank of Petroleum Resin

Amount of maleic anhydride g (mole)[b]	Conversion of maleic anhydride (%)[c]	Copolymerized product (g)	Color rank of petroleum resin G[d]
4 (0.041)	54	0.7	5
3 (0.031)	31	0.4	6
2 (0.020)	-[e]		7-8

[a] The reaction was carried out at 100°C for 4 hr under a nitrogen atmosphere.

[b] Amount of maleic anhydride versus starting material (100 g) was used.

[c] Conversion of maleic anhydride was calculated from unreacted maleic anhydride left in the reaction mixture by IR spectra at the absorbance 1860 cm^{-1}.

[d] Color rank was measured by the Gardner scale.

[e] No product.

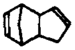
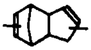
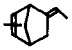
the investigation, the starting material was reacted with maleic anhydride, followed by hydrolysis with aqueous NaOH to transfer some products reacted with maleic anhydride into the aqueous layer and separation of the layer to obtain an oil layer. There is a difference of one rank in the color rank between the polymer obtained by cationic polymerization of the oil itself and the polymer produced by the same procedure from the fractions obtained from vacuum distillation of the oil. The main component of the residue gained from the vacuum distillation of the oil was naphthalene, which might be related to the color of the resin, by analysis of GLPC. The results of these experiments are shown in Table 2. Next as a model, the polymerization of styrene in the presence of each of the components shown in Table 2 was carried out to examine the color of polystyrene. The results are shown in Table 3.

Norbornadiene and ethylidene norbornadiene are also color components, and naphthalene itself is not but it acts as one in the presence of some color components.

We wished to resolve the problem of why the color of the petroleum resin appears from these components. It is clear that the color of the resin is attributed to the absorbance of the π-π^* transition in some long conjugated systems of a molecule.

Cyclopentadiene and methylcyclopentadiene were selected as

TABLE 2. Color Components and their Conversions by Diels-Alder Reaction or Copolymerization with Maleic Anhydride[a]

Components	Amount present in starting material (%)[b]	Conversion (%)[c]
	0.24	100
	0.19	100
	1.55	22.5
	0.59	14
	0.50	80
	0.10	75

[a] Reaction carried out with starting material (100 g) and maleic anhydride (3 g, 0.031 mole) at 100°C for 4 hr.

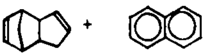
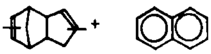
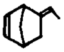
[b] The indicated amount of each component in the starting material becomes twice as much as that in polymerizable components which occupy half the amount of starting material.

[c] Conversion was calculated from the ratio of a component of the fractions obtained by vacuum distillation of the reaction mixture to the same component involved in the starting material.

representative color components. The cationic polymerization of styrene monomer with different amounts of each of the two in the presence of BF_3HOPh was carried out to determine the color change of polystyrene, and some activated species through the polymerization, which are trapped by 2,4,6-tri-tert-butyl nitrosobenzene used as a radical trapping agent [6], were examined by use of ESR spectroscopy to find some structure of a long conjugated system in the polymer. The influence of different amounts of cyclopentadiene and methylcyclopentadiene in styrene monomer on the color of polystyrene is shown in Fig. 1. It is shown that methylcyclopentadiene affects the color of polystyrene more than does cyclopentadiene, and the methyl group of methylcyclopentadiene seems to have something to do with the color of the polymer or conjugated systems.

Some activated intermediates of the polymerization were investigated by the method mentioned above. The results are shown in

TABLE 3. Color of Polystyrene as due to Color Components[a]

Components[b]	Color (G)
	8
	9[c]
	9+
	9-10
	4
	8
	1-2
	2
	5
	6-7

[a] Polystyrene obtained by polymerization the mixture of styrene (20 g, 0.2 mole) and toluene (60 g, 0.74 mole) with 0.55 mmole of BF_3HOPh at 35°C for 2 hr.

[b] Amount (6 mmole) of each component was added to styrene monomer.

[c] Naphthalene is not a color component, but in the presence of other color components, it acts as a color component.

Fig. 2. There are two kinds of radical species in both cases: one is a styryl radical [7, 8]; the other involves terminal radicals of long conjugated systems. Figure 3 shows the change of signal intensity of these radicals with time. It is very interesting that the signal intensity of the terminal radicals of long conjugated systems in the case of methylcyclopentadiene is greater than that in the case of cyclopentadiene, which is consistent with the data from Fig. 2, and that its intensity in the case of methylcyclopentadiene becomes a maximum in the range of a rapid decrease of the styryl radical;

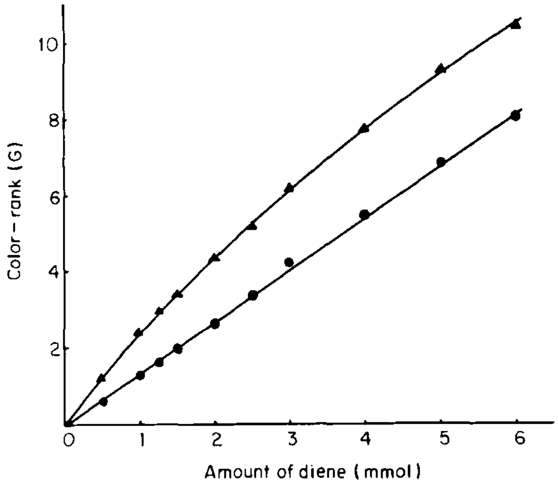


FIG. 1. Influence of different amounts of cyclopentadiene and methylcyclopentadiene in styrene monomer on the color of polystyrene: (●) cyclopentadiene; (▲) methylcyclopentadiene. Polymerization was carried out on a mixture of styrene (20 g, 0.2 mole) and toluene (60 g, 0.74 mole) in the presence of BF_3HOPh (0.55 mole) at 35°C for 2 hr. Color rank was measured by the Gardner scale.

that is, the polymerization of styrene monomer is preferred to formation of some conjugated systems. Near the end of the polymerization, the conjugated systems begin to form. From these data, it is assumed that some conjugated systems have the structure and formed through the mechanism shown in Fig. 4.

A propagating styryl radical extracts a hydrogen radical from a cyclopentadiene to form a cyclopentadienyl radical [9] attacking the aromatic ring of a styrene or a propagating polystyrene. A radical intermediate (a or a') expels a hydrogen radical to form a cyclopentadienyl compound (b or b'). The hydrogen on the cyclopentadiene at a benzylic position to the aromatic ring is very active [10] migrating to the ring of cyclopentadiene, with subsequent formation of conjugated system with the aromatic ring. In a similar manner, this species (c or c') further attacks the aromatic ring of another styrene to form a longer conjugated structure (d or d'). If a naphthalene is present, a structure (e) involving naphthalene may be produced.

An alternate mechanism is considered is shown in Fig. 5. A cyclopentadienyl radical is coupled with a quinoid radical [11] isomerized from a propagating styryl radical, reacting with another

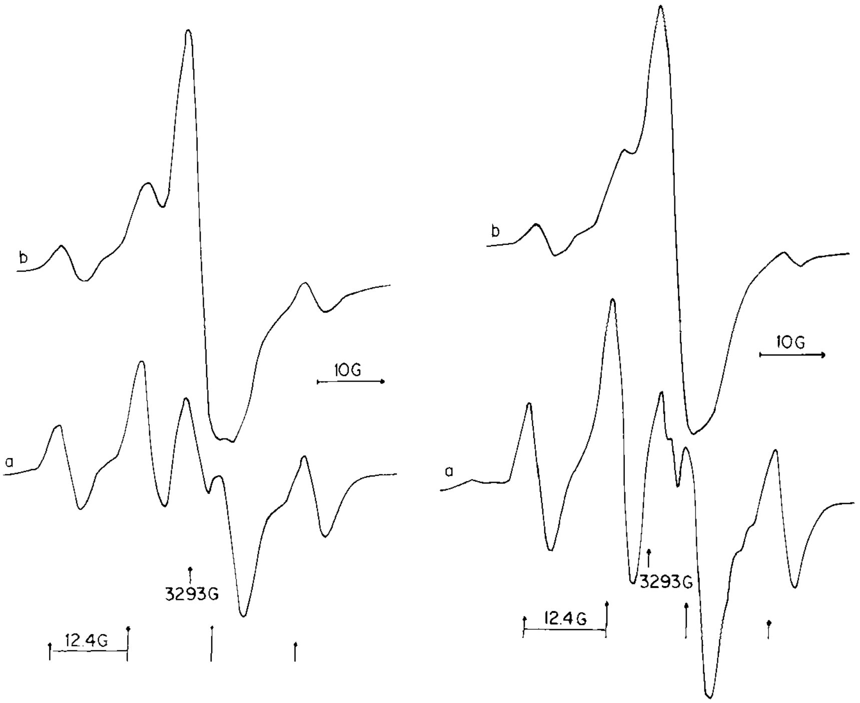


FIG. 2. ESR spectra of radical species in the presence of BF_3HOPh: (left) in cyclopentadiene and styrene and (right) in methylcyclopentadiene and styrene: (a) styryl radical quartet signal (1:3:3:1), a = 12.4 G; (b) conjugated radical. The reactions were carried out in an ESR sample tube with the diene (0.4 mmole), n-hexane (45 mmole), styrene (4.8 mmole), and BF_3HOPh (2.0×10^{-2} mmole) under nitrogen at 25°C. After the reaction, 2,4,6-tri-tert-butylnitrobenzene (1.0×10^{-2} mmole) was added to trap the radical species measured by ESR spectroscopy.

styrene to afford a similar structure. In addition, such a crosslinked structure of cyclopentadiene is proved from gelation in the polymerization of cyclopentadiene and olefinic compounds.

In the case of methylcyclopentadiene, there are three isomers, isomers 2 and 3 being more stable [12] from the point of view with the conjugated energy. The methyl groups of the two isomers are liable to form radicals, and therefore the efficiency of regenerating radicals in methylcyclopentadiene is greater than that in cyclopentadiene. A long conjugated structure in the case of methylcyclopentadiene

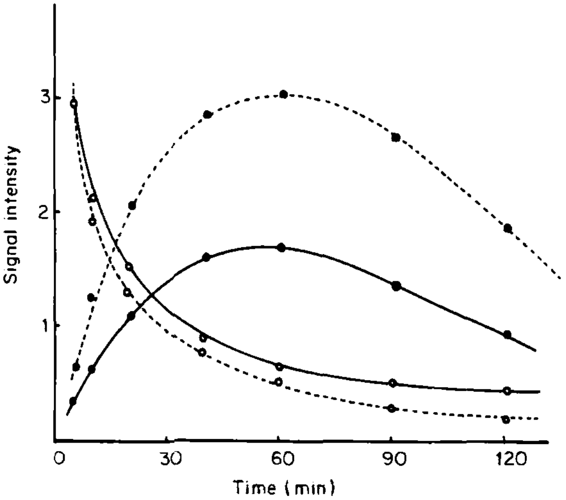


FIG. 3. Change of signal intensity of radical species vs. time in the case of cyclopentadiene and styrene and methylcyclopentadiene and styrene in the presence of BF_3HOPh: (○) styryl radical; (●) conjugated radical; (—) cyclopentadiene-styrene; (--) methylcyclopentadiene-styrene. The reactions were carried out in the ESR sample tube with the diene (0.4 mmole), n-hexane (45 mmole), styrene (4.8 mmole), and BF_3HOPh (2.0×10^{-2} mmole) at 25°C for periods of 5, 20, 40, 60, 90, and 120 min. After the reaction, 2,4,6-tri-tert-butylnitrobenzene (1.0×10^{-2} mmole) was added to trap the radical specie measured by ESR spectroscopy.

may be the structure shown in Fig. 6, formed in a similar manner as in the case of cyclopentadiene.

From the above considerations, it was concluded that some long conjugated structures which color the polymer are formed through the attack of cyclopentadiene or methylcyclopentadiene on an aromatic ring and that the structures are given as indicated in Figs. 4-6.

Last, the problem of the stability of cyclopentadiene and methylcyclopentadiene as monomers was investigated. These compounds usually exist as each of the dimers or Diels-Alder adducts [13] with other olefins. If this is so, the question remains, why a dimer can undergo reaction with maleic anhydride as a monomer and give an adduct even at room temperature. To elucidate this, the following experiment was carried out. The ordinary content of cyclopentadiene and methylcyclopentadiene in the starting material formed from

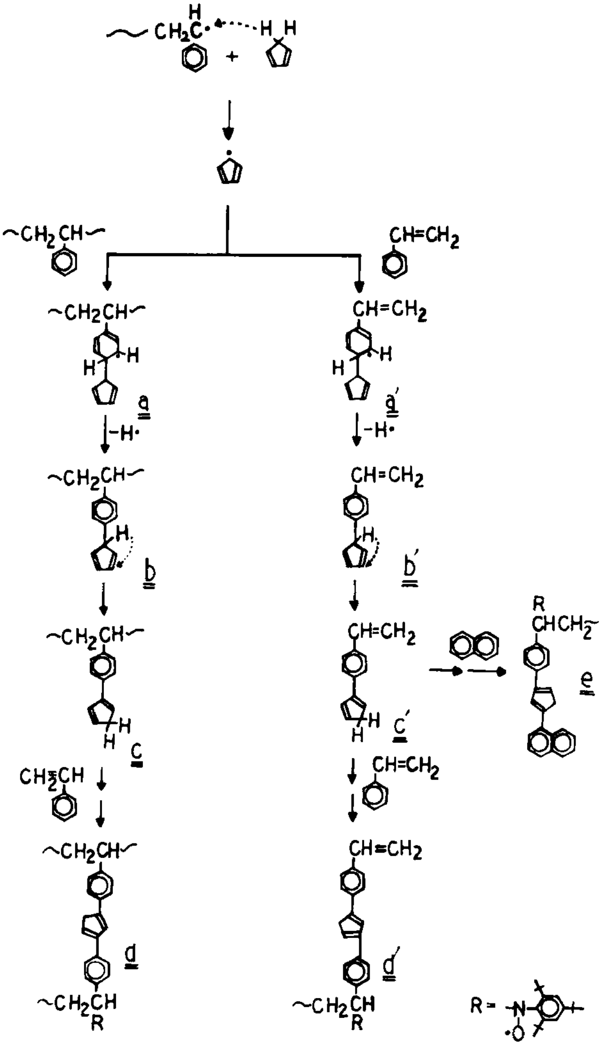


FIG. 4. Mechanism of formation of a long conjugated structure in the presence of BF_3HOPh.

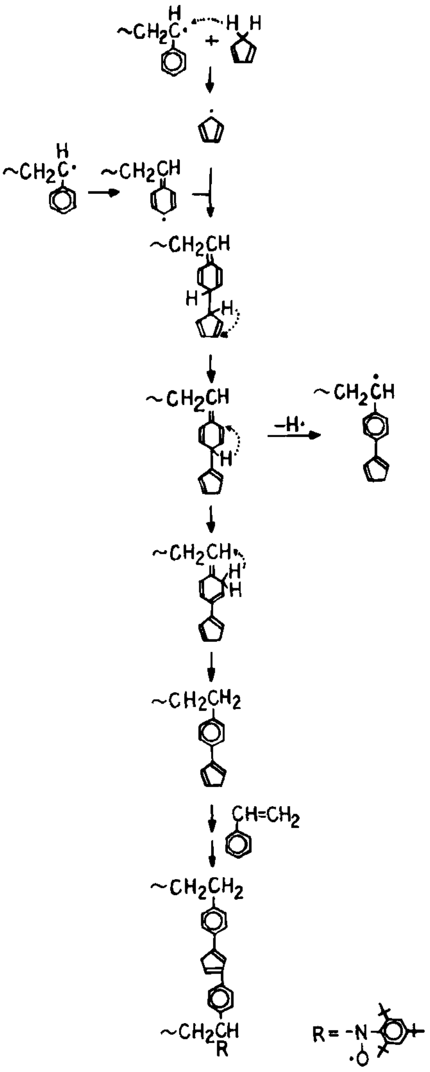


FIG. 5. Mechanism of formation of a long conjugated structure derived from a quinoid radical of a propagating styryl radical.

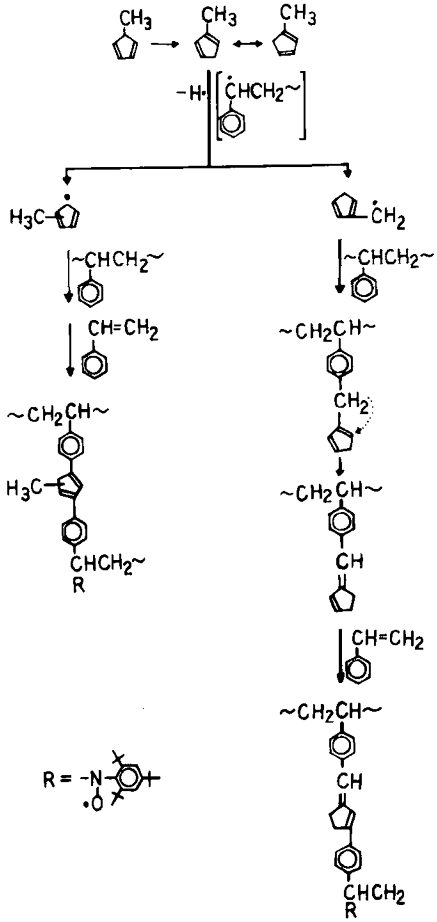


FIG. 6. Mechanism of formation of a long conjugated structure in the case of methylcyclopentadiene.

cracking, refining and reforming petroleum is below 1%. Then as a model, a styrene solution containing 1% each of the two dienes was prepared, and its change with time was examined by use of GLPC. The result showed that cyclopentadiene and methylcyclopentadiene exist as monomers even at room temperature for 24 hr even at a level of dilution of 1%. Therefore Diels-Alder adducts with maleic anhydride are formed from the monomers but not from their dimers.

EXPERIMENTAL

The infrared spectra were obtained by using a Nippon Bunko Model DS-701 D spectrometer.

The gas chromatographic analysis was performed on a Hitachi Model 073 gas chromatograph which is set with a flammable ionized detector and a 300 ft × 0.01 in. column packed with m-diphenoxybenzene. The inlet temperature was 220°C, the column temperature 110°C; the N_2 carrier gas flow rate was 1 ml/min and H_2, 0.5 ml/min.

The ESR spectra were measured by use of a Nippon Denshi JES-ME-360 instrument which is set with the following conditions: 25°C, field intensity 3190 ± 50 G, gain 5.0 × 10, response 0.01 sec, mod. width 1 G, power 8 mW, crystal current 0.4 mA.

Cyclopentadiene and Methylcyclopentadiene

Cyclopentadiene and methylcyclopentadiene were prepared by pyrolysis of their dimers at 180°C and 190°C, respectively.

Copolymerized Product of the Starting Material with Maleic Anhydride

Maleic anhydride was added to the starting material preheated at 100°C, and the mixture was reacted for 4 hr at this temperature. After the reaction, the reaction mixture was cooled at room temperature and filtered to separate out the copolymerized product. It was washed with toluene, dried in vacuo, and weighed.

Preparation of the Refined Fractions from the Starting Material

Maleic anhydride (3 g, 0.031 mole) was added to the starting material (100 g) preheated at 100°C, and the reaction was carried out at the same temperature for 4 hr under nitrogen. The reaction mixture was subjected to vacuum distillation at 150°C under a reduced pressure of 15 Torr to obtain the refined fractions.

Polymerization of Styrene Monomer in the Presence of Color Components

The polymerization of the mixture of styrene (20 g, 0.2 mole), toluene (60 g, 0.74 mole), and a color component (6 mmole) was carried out with 0.55 mmole of BF_3HOPh at 35°C for 2 hr under nitrogen. The polymerized solution was deactivated by addition of a mixture of calcium hydroxide and 10% aqueous sodium hydroxide (4:1) and filtered to obtain a solution containing the polymer. The solution was distilled at 210°C under reduced pressure (5 Torr) for 30 min to afford the polystyrene yield 92-93 mole %.

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