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Structural Characterization of Plasma-Polymerized Hydrocarbons

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ABSTRACT

Oils and films were produced by passage of ethylene, acetylene, and butadiene gases as well as benzene vapor through a radio-frequency electric discharge. The hydrocarbon oils produced in the plasma were dissolved in carbon tetrachloride and were analyzed by infrared and nuclear magnetic resonance spectroscopy. Based on these analyses, concentrations of characteristic functional groups were determined and used to propose molecular structures. The hydrocarbon oils are postulated to consist of irregular sequences of highly branched and incompletely crosslinked aliphatic backbone chains with pendant aromatic rings. Double bonds are interspersed along the chains. Hydrogen/carbon ratios in the proposed structures are consistent with the results from elemental analyses. Products from pyrolysis mass spectrometry can also be interpreted on the basis of the proposed structures. Similar techniques are used to analyze the structures of insoluble plasma polymerized films obtained from the same hydrocarbons. The major distinguishing feature in the films is the very high degree of crosslinking; of the order of one crosslink per six to ten chain carbon atoms.

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INTRODUCTION

Passage of an organic or organometallic vapor through a plasma sustained by a glow discharge often produces liquid or solid products. The process is referred to as plasma polymerization. However, plasma-polymerized materials differ significantly in structure and properties from those produced by conventional polymerization techniques. Plasma-polymerized materials generally are amorphous, highly crosslinked, and in most instances do not bear a simple relation in stoichiometry to the monomers.

Because of their irregular structure, the physical and chemical characterization of plasma polymerized materials is quite difficult. By means of IR, NMR, ESR, and UV spectroscopy [1-4] it has been possible to identify the nature of the functional groups present in the polymer, but more detailed descriptions of the polymer structure have yet to be developed. In the present paper a method based on the analysis of IR and NMR spectra is proposed for defining the concentrations of the functional groups present in these materials. This method is used to characterize the polymer oils and films obtained from ethylene, an ethylene-acetylene mixture, butadiene, and benzene. Hypothetical structures deduced from these analyses are compared with the results from pyrolysis mass spectra and elemental analyses.

EXPERIMENTAL

The apparatus used to prepare the polymer samples for this work has been described in a previous publication [5]. The major component of this apparatus is an evacuable bell jar containing two parallel circular electrodes. Power for the discharge was supplied by an International Plasma Corporation Model 3001 rf generator which operates at 13.56 MHz and delivers up to 150 W. Polymer was deposited either on pieces of aluminum foil or NaCl crystals, which were positioned approximately 2 in. from the center of the lower electrode. The temperature of this electrode was maintained near 20°C by circulation of cold water.

CP grade ethylene, acetylene, and butadiene were obtained from the Matheson Gas Co., and CP grade benzene was obtained from the Mallinckrodt Co. Each of these monomers was used without additional purification to produce both a high molecular weight oil and a solid film. The pressure, monomer flow rate, and discharge power used for each monomer are summarized in Table 1.

TABLE 1. Polymerization Conditions

Monomer	Monomer flow rate (STP cm ³ /min)	Pressure (Torr)	Power (W)	Polymer form
Ethylene	40	5.0	95	Oil
	80	2.0	85	Film
Ethylene-acetylene	50 (Ethylene)+ 8 (acetylene)	5.0	95	Oil
	80 (Ethylene) + 12 (acetylene)	1.8	100	Film
Butadiene	40	5.0	80	Oil
	25	1.5	80	Film
Benzene	6	3.5	30	Oil
	6	1.1	30	Film

Both the oil and film products obtained from each monomer were characterized by infrared spectroscopy and elemental analysis. In addition, the oil samples were characterized by proton magnetic resonance and pyrolysis mass spectrometry. Infrared spectra of samples deposited on NaCl crystals were recorded with a Perkin-Elmer Model 137 spectrophotometer. NMR spectra of the oil samples were taken on a Varian Model T-60 spectrometer. Mass spectra of the pyrolyzate obtained at 200°C were recorded by using an AEI Model MS12 spectrometer. For some of the infrared work and all of the NMR studies, solutions of the oil-type products in spectral grade carbon tetrachloride (Allied Chemical) were prepared. Elemental analyses of the samples to determine their carbon and hydrogen content were performed by combustion.

RESULTS AND DISCUSSION

Characterization of Oils Produced by Plasma Polymerization

Figure 1 illustrates the infrared spectrum for a sample of plasma polymerized oil prepared from ethylene. Since all of the monomers

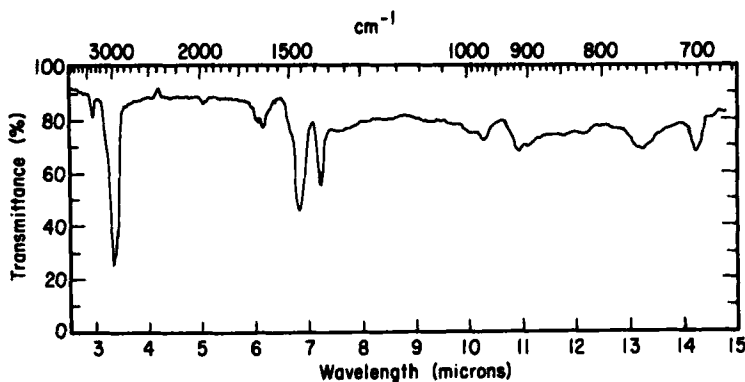


FIG. 1. Infrared spectrum of the oil produced by plasma polymerization of ethylene.

used in this work produced oils whose spectra were qualitatively alike, the interpretation of the spectrum in Fig. 1 can be applied to the spectra of the oils obtained from the other monomers. The assignment of the bands observed in Fig. 1 to specific modes of vibration is shown in Table 2. These assignments were made largely on the basis of tabulated data [6-8]. With the exception of the bands at 1370, 752, and 700 cm^{-1} , these assignments are identical to those reported previously [5].

The band at 1370 cm^{-1} was originally assigned to methylene bending vibrations on the basis of the occurrence of a similar band in the spectrum of polyethylene at 1369 cm^{-1} [9]. A reexamination of this assignment was undertaken in the course of the present investigation. It was concluded on the basis of the correlation of the intensity of the 1370 cm^{-1} band with the intensity of a band corresponding to methyl groups appearing in the NMR spectra of the oils (see the discussion given below) that the 1370 cm^{-1} band is best assigned to bending vibrations of methyl groups. It is noted for the sake of comparison that the corresponding vibrations occur in polyethylene at 1373 cm^{-1} .

The bands at 752 and 700 cm^{-1} were originally assigned to rocking vibrations associated with a sequence of methylene groups. In the present work it was determined that these bands correlate strongly with the intensity of the bands for phenyl groups observed in the NMR spectra. This correlation suggests that the bands at 752 and 700 cm^{-1}

TABLE 2. Assignment of Infrared Absorption Bands

Absorption frequency ν (cm^{-1})	Assignment
3400	O-H stretch
3000	C-H stretch in $\text{C}=\text{C}-\text{H}$
2940 } 2880 }	C-H stretch in CH_2 , CH_3
1960	C=C stretch in $\text{C}=\text{C}=\text{C}$
1670 } 1640 }	C=C stretch (nonconjugated)
1605	C=C stretch (conjugated)
1495	C-C stretch in $-\text{C}_6\text{H}_5$
1455	C-H bend in CH_2
1447	C-H bend in CH_3
1370	C-H bend in CH_3
990	C-H out-of-plane deformation in $-\text{C}=\text{CH}_2$
965	C-H out-of-plane deformation in $-\text{C}=\text{C}-$ (trans)
905	C-H out-of-plane deformation in $-\text{C}=\text{CH}_2$
752 } 700 }	C-H bend in monosubstituted phenyl group $\text{C}_6\text{H}_5-\text{R}$

are more properly assigned to C-H vibrations on monosubstituted phenyl groups as indicated in Table 2.

For quantitative analysis of the infrared spectra, CCl_4 solutions containing approximately 2% by weight of each oil were prepared. The spectra obtained for the oils derived from ethylene, an ethylene-acetylene mixture, butadiene, and benzene are shown in Fig. 2. The bands for the bending vibrations of methylene and methyl groups which occur at 1455 and 1370 cm^{-1} , respectively, can be seen clearly and are not obscured by various C-Cl absorptions. The band for bending vibrations of hydrogen atoms on phenyl groups appears as a sharp

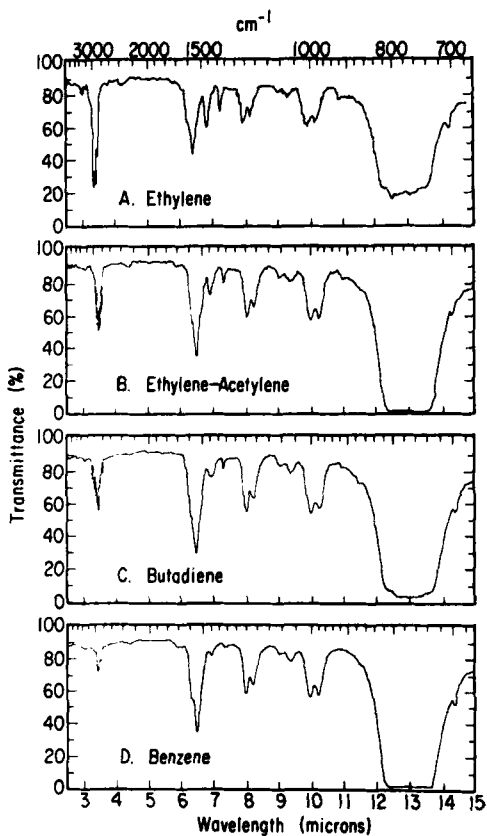


FIG. 2. Infrared spectra of CCl_4 solutions of oils produced in a plasma: (A) ethylene; (B) ethylene-acetylene; (C) butadiene; (D) benzene.

shoulder at 700 cm^{-1} on the broad C-Cl band centered at 780 cm^{-1} . Peaks indicating unsaturation are generally masked by solvent absorption and therefore cannot be detected.

NMR spectra of approximately 4% by weight CCl_4 solutions of the oils produced in the plasma are shown in Fig. 3. As assignment of the NMR peaks is given in Table 3 based upon tabulated data [10]. Aromatic proton absorption ($\delta \approx 7.04$) is clearly shown in the spectra of all four plasma polymerized oils and is extremely strong for the one

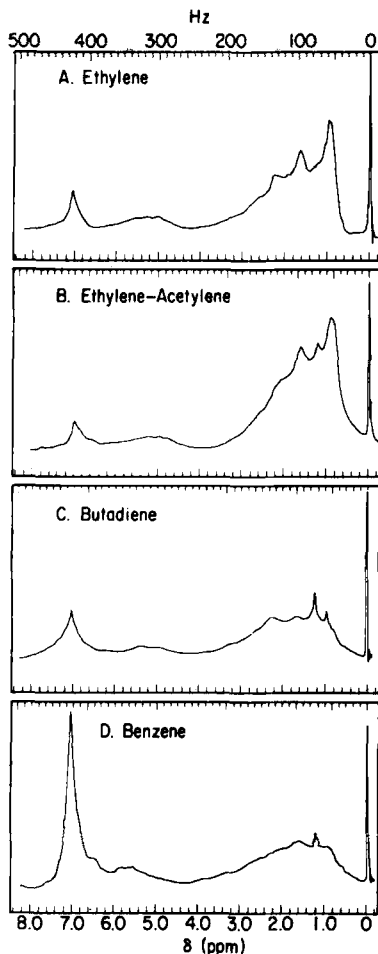


FIG. 3. NMR spectra of CCl_4 solutions of oils produced in a plasma: (A) ethylene; (B) ethylene-acetylene; (C) butadiene; (D) benzene.

derived from benzene. Aliphatic and vinyl proton peaks are also observed in each case, although the vinyl proton peak is broad and not very intense. The spectrum for the benzene-derived oil (Fig. 3D) is similar to that published by Neiswender [2] but contains greater detail.

TABLE 3. Assignment of NMR Absorption Bands

Chemical shift δ (ppm)	Assignment
0.96	R-CH ₃
1.26	R-CH ₂ -R
1.61	R ₂ -CH-R
1.91	-C=C-CH ₂ -R
2.31	C ₆ H ₅ -CH ₂ -R
5.01	Various $\begin{array}{c} \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \\ \text{H} \end{array}$
5.26	
5.41	
6.14	$\begin{array}{c} \text{H} \\ \\ -\text{C}=\text{C}-\text{C}=\text{C}- \\ \\ \text{H} \end{array}$
7.04	C ₆ H ₅ -H

Many of the structural features identified from an interpretation of the IR and NMR spectra were confirmed by mass spectra taken of the products obtained by pyrolysis of the oils at 200° C. Figure 4 illustrates the spectrum for the pyrolyzate obtained from the ethylene-derived oil, and an interpretation of the major peaks observed in the

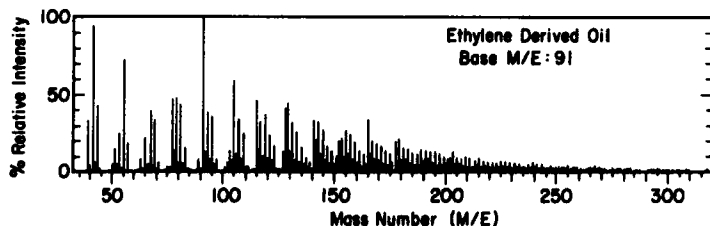


FIG. 4. Pyrolysis mass spectrum of oil produced by plasma polymerization of ethylene.

mass spectra based on published data [11-13] is given in Table 4. The pyrolyzate of each oil contains aliphatic, olefinic, and singly substituted phenyl groups. The most intense peak in each spectrum is that occurring at mass 91 and can be identified with a tropylium ion fragment. While all of the spectra show evidence of aromatic groups, the intensities of the corresponding peaks are larger for the oils derived from butadiene and benzene and smaller for those derived from ethylene and the ethylene-acetylene mixture. Correspondingly, the spectra for the latter two monomers show larger concentrations of aliphatic and olefinic groups. It should be noted that a part of the olefinic structure observed in the pyrolyzate may be formed by cracking of the oil structure at tertiary carbon sites. Therefore the level of unsaturation observed in the mass spectra is likely to be higher than that actually present in the oils.

The identification of methyl, methylene, tertiary carbon, and olefinic groups in the plasma-produced oils is not surprising and is consistent with the observations of previous investigators [14]. The observation of significant aromatic character, although unanticipated, is not in conflict with what is known of the organic chemistry which transpires in a plasma. In the work of Kobayashi et al. [15] it was shown that ethylene and butadiene form significant amounts of acetylene while undergoing polymerization, and it was suggested that this might be a key step in the polymerization process. The formation of acetylene can then explain the formation of phenyl groups, since acetylene has been observed to form benzene, styrene, and phenylacetylene upon reaction in a discharge [16, 17]. Reaction of the styrene or phenylacetylene with free radicals would then lead to an incorporation of phenyl groups into the molecular structure of the oil. Likewise, any benzene present, either as the result of its introduction as a monomer or formation via acetylene, could be converted into a phenyl radical which could then react with radicals or sites of unsaturation in the developing oil macromolecule. Both of these pathways would explain why only monosubstituted rings are found in the oils.

To further elucidate the molecular structure of the oils, a procedure was developed for obtaining a quantitative measure of the number of moles of each functional group present per gram of oil. Implementation of this procedure requires a simultaneous utilization of the IR and NMR spectra.

The concentrations of methylene, methyl, and phenyl groups were obtained by applying the Beer-Lambert Law to the infrared bands appearing at 1455, 1370, and 700 cm^{-1} . Because of the complexity and uncertainty of the molecular structure of the oils, it was not possible to obtain extinction coefficients for each of the bands by

TABLE 4. Intensities of Major Peaks in Pyrolysis Mass Spectra of Oils Produced by Plasma Polymerization

Group	Formula	Mass number	Relative intensity (% of total)				
			Ethylene	Ethylene-acetylene	Butadiene	Benzene	
Alkane	$C_n H_{2n+1}$	43	1.66	1.58	0.09	0.55	
		57	0.74	.86	0	0.45	
Monounsaturated alkyl	$C_n H_{2n-1}$	41	3.66	3.49	2.18	1.31	
		55	2.79	2.63	0.86	1.00	
		69	1.30	1.40	0.14	0.72	
Diunsaturated alkyl	$C_n H_{2n-3}$	83	0.68	0.69	0.16	0.54	
		39	1.30	1.49	2.44	2.26	
		53	1.00	1.04	2.43	0.69	
		67	1.54	1.52	0.59	1.29	
		81	1.69	1.65	0.53	0.67	
Triunsaturated alkyl	$C_n H_{2n-5}$	95	1.44	1.50	0.28	0.76	
		109	0.95	0.94	0.12	0.21	
		123	0.61	0.58	0	0.17	
		51	0.59	0.62	1.69	2.00	
		65	0.84	0.95	1.46	1.26	

	79	1.86	1.85	1.46	1.17
	93	1.46	1.50	0.82	0.37
	107	1.30	1.24	0.44	0.29
	121	0.91	0.88	0.11	0.17
	135	0.62	0.65	0	0.08
Phenyl alkane or quarternary unsaturated alkyl	77	1.81	1.86	2.46	2.85
	91	3.86	3.60	4.87	4.63
	105	2.28	2.28	1.71	2.31
	119	1.44	1.34	0.56	0.37
	133	0.99	0.92	0.22	0.18
	147	0.64	0.63	0.12	0.08
Phenyl mono- unsaturated alkyl	117	1.26	1.28	1.30	1.01
	131	1.27	1.28	1.54	0.62
	145	1.07	1.05	0.74	0.33
	159	0.75	0.77	0.24	0.15
Phenyl-diunsaturated alkyl	115	1.76	1.86	4.41	2.60
	128 + 129	3.32	3.31	7.51	3.22
	143	1.24	1.30	1.95	0.81
	157	0.93	0.98	0.99	0.54

(continued)

TABLE 4 (continued)

Group	Formula	Mass number	Relative intensity (% of total)				
			Ethylene	Ethylene-acetylene	Butadiene	Benzene	
Phenyl-triunsaturated alkyl	$C_6H_5C_nH_{2n-6}$	127	0.51	0.51	1.25	0.56	
		141	1.26	1.29	3.02	1.12	
		154 + 155	1.43	1.50	2.93	2.92	
		169	0.71	0.69	1.18	0.35	
		183	0.57	0.59	0.63	0.24	
		197	0.44	0.38	0.19	0.07	
Phenyl-quarternary unsaturated alkyl		139	0.24	0.22	0.82	0.56	
		152 + 153	1.60	1.60	5.19	2.52	
		167	0.76	0.75	2.45	1.22	
		181	0.60	0.52	1.17	0.52	

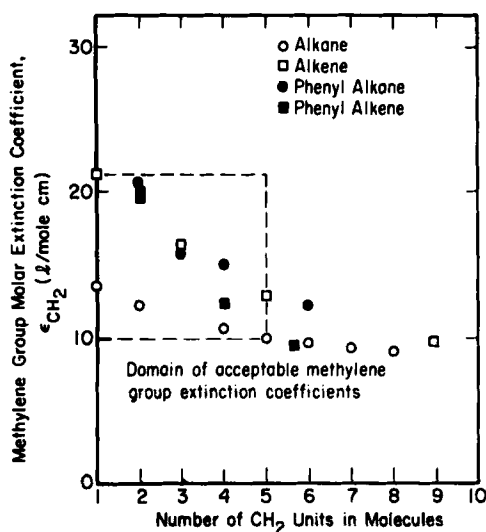


FIG. 5. Molar extinction coefficients for methylene group bending vibration (1455 cm^{-1}).

standard techniques [18] or reference to the literature. As a result it was necessary to evaluate these extinction coefficients by examination of the values for similar groups appearing in a variety of structural environments.

Figure 5 illustrates published extinction coefficients [19, 20] for methylene bending vibrations in alkanes, alkenes, phenyl alkanes, and phenyl alkenes. These families of compounds were selected because they most closely simulate the molecular environment of the methylene groups occurring in the plasma-polymerized oils. In Fig. 5 the extinction coefficients for each family of compounds are plotted as a function of the number of methylene groups present in the compound, to accentuate the dependence of the extinction coefficient on this number. Because the extinction coefficients show a substantial spread in values depending on which family of compounds is chosen and the number of methylene groups in a particular molecule, an averaging procedure was adopted. From previous studies [21] of the structure of plasma-polymerized hydrocarbons it was established that the polymer would contain roughly 1 to 5 methylene groups between branch or crosslink points. As a result, it was decided to use an

TABLE 5. Functional Group Concentrations in Hydrocarbon Oils Produced by Plasma Polymerization^a

Monomer	[RCH ₃]	[R ₂ CH ₂]	[R ₃ CH]	[C=C]	[CH ₃]/[C ₆ H ₅]	
					[C ₆ H ₅]	IR NMR
Ethylene	8.3	17.0	9.5	3.5	1.2	6.9 6.6
Ethylene-acetylene	8.9	17.0	10.0	3.5	1.2	7.5 7.3
Butadiene	5.6	15.0	5.9	4.5	2.6	2.1 1.9
Benzene	5.9	19.0	18.0	6.1	11.0	0.51 0.59

^a Estimated error in functional group concentrations if 10-15%.

arithmetic average of the extinction coefficients appearing in Fig. 5 for compounds containing 5 or less methylene groups. By this means, a value of $\epsilon_{\text{CH}_2} = 14.9$ liter/mole-cm was obtained. The concentrations of methylene groups in each of the oils is given in Table 5.

A somewhat different technique was used to calculate the extinction coefficients for methyl and phenyl groups. Here again, it was found desirable to start by identifying the range of extinction coefficients observed for families of known compounds. These data are shown in Figs. 6 and 7 plotted as a function of the number of methylene groups present in the molecules. As an additional piece of information, the molar ratio of methyl to phenyl groups was determined from the NMR spectrum of the oil derived from ethylene. Values of the extinction coefficients for methyl and phenyl groups were then chosen and used together with the absorbance values of the 1370 and 700 cm^{-1} peaks to determine the molar ratio of methyl to phenyl groups in the ethylene

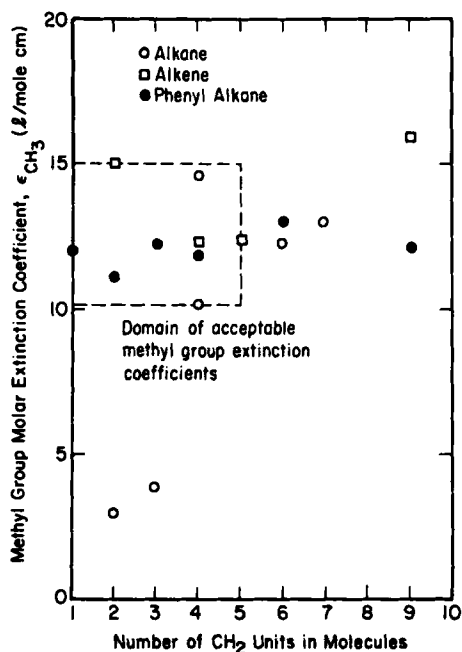


FIG. 6. Molar extinction coefficients for methyl group bending vibration (1370 cm^{-1}).

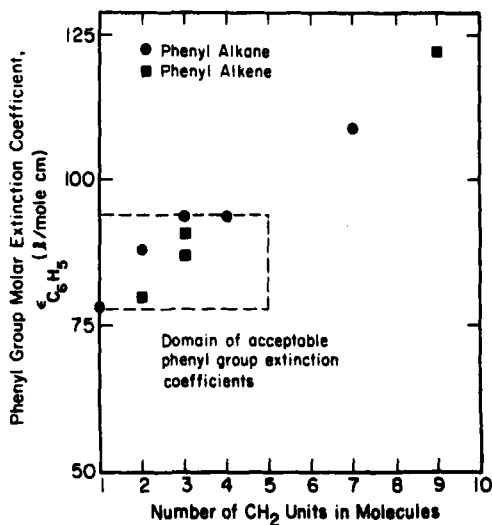


FIG. 7. Molar extinction coefficients for C-H bending vibration in monosubstituted phenyl group (700 cm^{-1}).

derived oil. If the ratio of these groups obtained from the IR data did not agree with that obtained from the NMR data, a new set of extinction coefficients was chosen. This procedure was repeated until the two ratios were in as close an agreement as possible consistent with the extinction coefficient values lying between the dashed lines shown on Figs. 6 and 7. The final values of the extinction coefficients obtained by this means were $\epsilon_{CH_3} = 15.0$ and $\epsilon_{C_6H_5} = 78.7$ liter/mole-cm. These same coefficients were then used to determine the concentrations of methyl and phenyl groups in all other oil samples. The results are listed in Table 5 together with the molar ratios of the two groups derived from the IR and NMR data. Notice that the ratios obtained from the two data sets are in close agreement in all cases, which strongly supports the method used to obtain the extinction coefficients.

The concentration of tertiary carbon groups is determined in the following way. First, the molar ratio of total aliphatic groups to phenyl groups is obtained through an integration of the appropriate peaks appearing in the NMR spectra. In performing this computation it is assumed that each aliphatic group contributed an average of two

hydrogen atoms. This assumption is supported by the final observation that the concentration of tertiary carbon groups is approximately equal to the concentration of methyl groups. The ratio is represented by $([-\overset{|}{\text{C}}\text{H}] + [-\text{CH}_2-] + [-\text{CH}_3])/[-\text{C}_6\text{H}_5]$, where $[x]$ denotes the number of moles of group x per gram of polymer. Using the concentrations of methyl, methylene, and phenyl groups determined from the infrared spectra, the concentration of tertiary carbon groups can then be determined. Table 5 lists the concentrations of tertiary carbon groups for each of the oil samples.

Finally, the concentration of olefinic groups was established by integration of the broad peak for these groups appearing in the NMR spectra. In performing these computations it was assumed that each $-\text{C}=\text{C}-$ group had associated with it an average of 2.0 hydrogen atoms. This assumption was based upon the consideration that while the IR spectra showed evidence of $-\text{CH}=\text{CH}-$ and $-\text{CH}=\text{CH}_2$ groups, the presence of $-\overset{|}{\text{C}}=\text{CH}-$ could not be totally ruled out. The computed concentrations of >C=C< groups are listed in Table 5.

Examination of Table 5 reveals that the primary difference between the four oils is the relative amount of aliphatic and aromatic character. The oils derived from ethylene and an ethylene-acetylene mixture are nearly identical and contain substantially greater aliphatic character than the oils derived from butadiene and benzene. The increase in aromatic character as one proceeds from ethylene to benzene is consistent with the expected ease with which phenyl groups might be formed from each monomer.

The concentrations of each functional group are also influenced by the monomer used to prepare the oil. There exists a well-defined increase in the concentrations of methylene, phenyl, and olefinic groups and a decrease in the concentration of methyl groups in going from ethylene to benzene. With the exception of the oil derived from butadiene, the concentration of tertiary carbon groups also increases from the top to the bottom of Table 5.

The data given in Table 5 can be used to postulate a molecular structure of the oil molecules provided that the molecular weight is known. In a previous study the molecular weight was determined to be about 600 g/mole for an ethylene-derived oil. With this information the molecular structure I was hypothesized. It must be stressed that the structure shown may not be complete, since no account has been taken of the possible existence of aliphatic rings or quaternary carbon atoms. Both of these features are undoubtedly present to some extent.

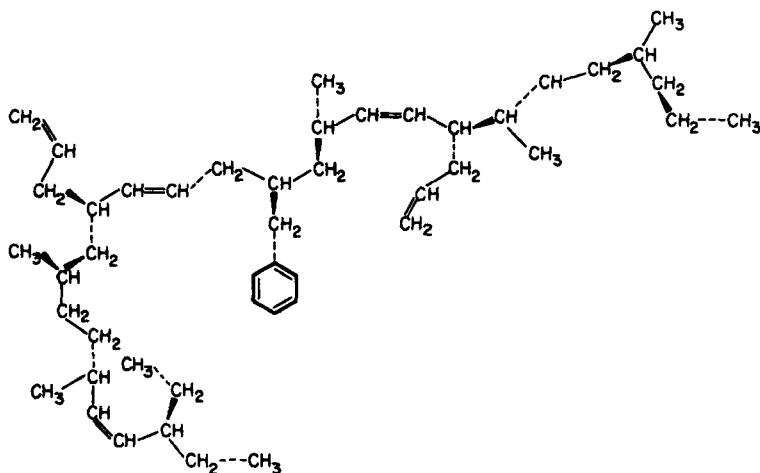


TABLE 6. Elemental Analysis of Hydrocarbons Oils Produced by Plasma Polymerization

Monomer	H/C Monomer	H/C Oil	H/C Proposed structure
Ethylene	2.0	1.41	1.62
Ethylene-acetylene	1.9	1.40	1.62
Butadiene	1.50	1.16	1.24
Benzene	1.0	0.92	1.07

Hypothetical structures for the remaining oils can also be drawn, but are not shown here since they are similar to I. In Table 6, a summary is made of the H/C ratio deduced for each of the postulated molecular structures. The true H/C ratio, taken from experimental measurements, is also provided, along with the H/C ratio of the monomer. It is to be noted that the hydrogen content of each oil is less than that of the corresponding monomer, and that the hydrogen content of the oils decrease as the hydrogen content of the monomer decreases. It is also observed that the hydrogen content of the proposed

oil structures is close to that found experimentally but always higher. This is not unexpected, since the postulated structures do not allow for quaternary carbons, cyclic structures, or free radical sites. The inclusion of each of these groups would reduce the H/C ratio of the postulated structures.

Characterization of Films Produced by Plasma Polymerization

In the preceding, we have shown that it is possible to deduce the structure of plasma-polymerized hydrocarbon oils on the basis of the combined information from IR and NMR data. NMR data were particularly useful in specifying some of the less clearly defined IR assignments. Since the plasma-polymerized films are not soluble in any solvent, NMR measurements are not possible. However, their IR spectra can still be obtained by depositing the film on NaCl crystals. We shall now use the techniques developed for the oils to elucidate the structure of plasma-polymerized films.

Figure 8 shows infrared spectra for plasma polymerized films derived from ethylene, an ethylene-acetylene mixture, butadiene, and benzene. No qualitative differences are observed between the spectra of the film and oil derived from the same monomer, and the spectra of all four films are quite similar.

The concentrations of methylene, methyl, and phenyl groups were determined from the infrared spectra using the molar extinction coefficients determined during characterization of the oils. In order to express the group concentrations on a per gram of polymer basis the density of each polymer was required. Values for the densities were taken from Mayhan [22]. The concentrations of methylene, methyl, and aromatic groups are presented in Table 7.

To evaluate the concentration of tertiary carbon groups it was assumed that

$$\begin{aligned} & ([-\text{CH}_3] + [-\text{CH}_2-] + [-\overset{|}{\text{C}}\text{H}])_{\text{film}} \\ & = ([-\text{CH}_3] + [-\text{CH}_2-] + [-\overset{|}{\text{C}}\text{H}])_{\text{oil}} \end{aligned} \quad (1)$$

This approximation should be valid, since the aliphatic groups comprise more than 85% of the total number of molecular groups in either the oil or the film. Since the right-hand side of the equality is already known, as are the concentrations of methylene and methyl groups in

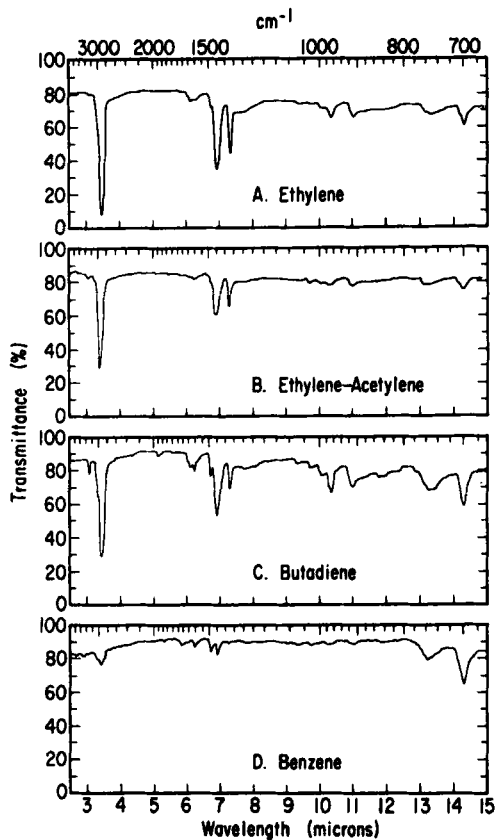


FIG. 8. Infrared spectra of films produced in a plasma: (A) ethylene; (B) ethylene-acetylene; (C) butadiene; (D) benzene.

the film, the concentration of tertiary carbon groups can easily be determined and are listed in Table 7.

The concentration of olefinic groups present in the films was determined through the use of a second approximation, Eq. (2).

$$\left[\text{>C=C<} \right]_{\text{film}} / \left[\text{>C=C<} \right]_{\text{oil}} = \left[\text{-C}_6\text{H}_5 \right]_{\text{film}} / \left[\text{-C}_6\text{H}_5 \right]_{\text{oil}} \quad (2)$$

TABLE 7. Functional Group Concentrations in Hydrocarbon Films Produced by Plasma Polymerization^a

Monomer	Functional group concentrations (mmole/g polymer)			
	[RCH ₃]	[R ₂ CH ₂]	[R ₃ CH]	[C=C]
Ethylene	6.2	10.0	18.0	1.1
Ethylene-acetylene	7.2	11.0	18.0	1.5
Butadiene	4.2	10.0	12.0	2.0
Benzene	2.7	14.0	26.0	4.4

^a Estimated error in functional group concentrations is 10-15%.

TABLE 8. Ratios of Infrared Bond Absorbances for Oils and Films Produced by Plasma Polymerization

Monomer	Ratio of infrared bond absorbances	
	965 cm ⁻¹ [(C=C)trans] _{film}	700 cm ⁻¹ [(C ₆ H ₅)] _{film}
Ethylene	0.71	0.68
Ethylene-acetylene	0.37	0.34
Butadiene	0.76	0.61
Benzene	0.25	0.31

To test the validity of the approximation, integrated intensities of the infrared bands occurring at 965, 905, and 700 cm^{-1} were obtained from the spectra for both the oil and film derived from each monomer. The bands at 965 and 905 correspond to bending vibrations in trans $-\text{CH}=\text{CH}-$ and $>\text{CH}=\text{CH}_2$ groups respectively while the band at 700 cm^{-1} corresponds to wagging vibrations in $-\text{C}_6\text{H}_5$ groups. For each absorption a ratio of the band intensity for the film to that for the oil was computed and the results are shown in Table 8. As can be seen, all three ratios for each monomer are reasonably close to each other. It was assumed that the observed level of agreement was sufficient to justify the original assumption. Using this assumption, olefinic group concentrations were determined for each film and are listed in Table 7.

Comparison of Tables 5 and 7 show that the methyl and methylene group concentrations are slightly lower in the film than in the oil, and that the olefinic group concentrations are about two to three times lower in the films. Conversely, the tertiary carbon concentrations are nearly twice as large in the film obtained from each monomer. These facts suggest that reactions leading to aromatization are suppressed somewhat during film formation while branching and crosslinking are greatly enhanced.

The extent of branching and crosslinking occurring in both the oils and the films can be estimated by the following means. If it is assumed that tertiary carbon atoms are the primary sites at which branching and crosslinking occurs, the number of backbone carbon atoms per branch point can be written as

$$\chi_b = \frac{[\text{CH}_3] + [\text{CH}_2] + [\text{CH}] + 2[\text{C}=\text{C}]}{[\text{CH}]} \quad (3)$$

Furthermore, since the concentrations of tertiary carbon atoms and methylene groups are comparable, one expects the concentration of tertiary carbon atoms to equal the sum of the terminal group concentrations in the case where no crosslinking takes place [Eq. (4)]

$$[\text{CH}] = [\text{CH}_3] + [\phi] \quad (4)$$

Where crosslinking does take place the number of backbone carbon atoms per crosslink can be expressed as

TABLE 9. Branching and Crosslink Densities of Plasma-Derived Oils and Films

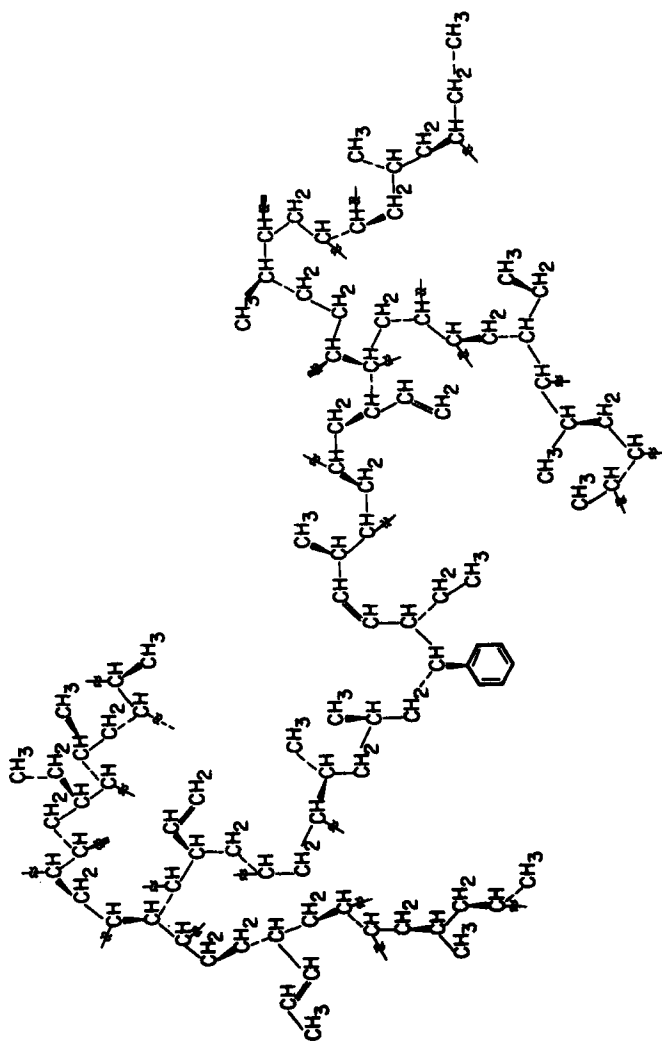
Monomer	Polymer form	χ_b	χ_c
Ethylene	Oil	4.4	∞
	Film	2.0	6.4
Ethylene-acetylene	Oil	4.4	∞
	Film	2.2	7.6
Butadiene	Oil	6.0	a
	Film	2.6	9.6
Benzene	Oil	3.1	∞
	Film	2.0	6.7

^aSee text.

$$\chi_c = \frac{2([\text{CH}_3] + [\text{CH}_2] + [\text{CH}] + 2[\text{C}=\text{C}])}{[\text{CH}] - [\text{CH}_3] - [\phi]} \quad (5)$$

In developing Eqs. (3) and (5), $-\overset{|}{\text{C}}=\text{CH}-$ groups have not been considered as possible branch points. The reason for this is that the total concentration $\text{>C}=\text{C}<$ groups is considerably smaller than the concentration of $-\overset{|}{\text{C}}\text{H}$ groups and the concentration of $-\overset{|}{\text{C}}=\text{CH}-$ groups is some fraction of the total concentration of $\text{>C}=\text{C}<$ groups. As a result, it is postulated that $-\overset{|}{\text{C}}=\text{CH}-$ groups can at best make only a small contribution to the extent of branching or crosslinking.

Calculated values of χ_b and χ_c are given in Table 9 for both the oil and the film products derived from each of the monomers. For each monomer the value of χ_b is noticeably larger for the oil than for the film. The values of χ_c calculated for the oils made from ethylene, an ethylene-acetylene mixture, and benzene are all extremely large and therefore set as infinity. This is a direct result of the equivalence of the tertiary carbon group concentration to the sum of the methyl and phenyl group concentrations. The oil derived from butadiene is different in that the concentration of tertiary carbon atoms is less



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than the concentration of terminal groups. This suggests that $-\overset{|}{\text{C}}=\text{CH}-$ groups may play a more significant role as branch points in this particular oil. Finally, it is noted that the value of χ_c for each of the films indicates that the films possess a crosslink density of one crosslink per six to ten backbone carbon atoms. This result is in rough agreement with previous estimates of the crosslink density deduced from dielectric measurements [21].

A molecular structure for a section of the film derived from ethylene is II. Here, as in the case of I, the structure has been based upon the computed distribution of functional groups which are listed in Table 7. The broken bands shown in structure II are crosslink points and connect to other portions of the film.

CONCLUSION

The present work has shown that the identification of the functional groups present in plasma-polymerized materials is facilitated when both IR and NMR spectra are available for the same sample. By combining these two forms of spectroscopy it has been demonstrated that the concentration of each functional group can be evaluated for plasma produced oils. While the procedure requires a number of assumptions, the results show an internal consistency and lead to H/C ratios in reasonably good agreement with those measured experimentally. The procedure used to characterize oils has been extended to the characterization of films. The analyses for the films show that they are more highly crosslinked than the oils and contain fewer methyl, methylene, olefin, and phenyl groups. Estimates of the crosslink density of the films reveal that there are six to ten backbone carbons per crosslink. By using the functional group analyses, hypothetical molecular structures have been constructed for both oils and films. Finally, it is believed that use of the procedures outlined here will be of assistance in furthering the interpretation of the physical and chemical properties of plasma-polymerized products.

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