Fractionation of Polyvinyl Chloride Pitch by Vacuum Sublimation

Mutsukazu KAMO, Hisao KANDA, Yoichiro SATO, and Nobuo SETAKA

National Institute for Researches in Inorganic Materials, Sakura-mura, Niihari-gun, Ibaraki 300-31

(Received July 23, 1973)

Pitch prepared by heating polyvinyl chloride at 400 °C (PVC pitch) was fractionated by vacuum sublimation. The fractions were studied by means of elementary analysis, determination of molecular weight, IR spectroscopy and NMR spectroscopy. It was found that each fraction has a characteristic constituent as follows: 1) Zones 1 and 2 are composed of some aromatic nuclei with 3—4 rings and 3—5 rings linked with aliphatic chains, respectively; 2) Zones 3 and 4 are composed of condensed aromatic nuclei with 6—8 rings and 6—7 rings, respectively; 3) In zone 5, aromatic nuclei have 2—4 aromatic rings on an average, and the ratio of the aliphatic group is higher than that of other zones; 4) The sublimation residue is mainly composed of condensed aromatic nuclei, and the ratio of aromatic hydrogen to aliphatic hydrogen in the residue is the highest.

The initial stage of carbonization of pitch can be studied by chemical methods until the optically anisotropic phase insoluble in usual organic solvents develops.[1] Since pitch is a multi-component system, solvent extraction and chromatographic methods are utilized for fractionation or separation in order to study the mechanism of carbonization.

In this work, vacuum sublimation was used for fractionation. The fractionation is carried out by the difference in vapor pressure. The vapor pressure decreases with increasing molecular weight in a homologous series.

Polyvinyl chloride(PVC) pitch was chosen, since investigations of the carbonization of PVC[2-6] show it to be suitable for examining the utility of vacuum sublimation. Aromatization of aliphatic components is an important process in carbonization and PVC pitch is a typical system prepared from aliphatic compound.

Each fraction obtained by vacuum sublimation was studied by means of elementary analysis, determination of molecular weight, IR spectroscopy and NMR spectroscopy. The results are discussed as regards size of aromatic nuclei, because carbonization is considered to be a process of the growth of aromatic nuclei.

Experimental

Preparation of PVC Pitch. PVC pitch was prepared by heating commercial polyvinyl chloride (Wako Pure Chem. Ind.) under a nitrogen stream at 400 °C. Heat treatment was carried out for 5 hr at 400 °C until the weight loss became constant. The yield was 23%.

Vacuum Sublimation. The heater of the vacuum sublimation furnace consists of two parts, one for sample heating and the other for separation, both of which can be controlled independently. The sublimation column made of a Pyrex glass tube, 8 mm inner diameter and sealed at one end, is connected to a vacuum system consisting of a rotary vacuum pump and monitored by a Pirani guage. Powdered sample, 300—400 mg, was charged in each run. Sublimation was performed at 390—395 °C at $5—6\times10^{-3}$ Torr as vacuum was attained at the end of each run.

Measurement of Molecular Weight. Number-average molecular weights of sublimed fractions in chloroform were determined at 34 °C with a Hitachi 115 vapor-pressure osmometer. Zone-refined benzil (Tokyo Chemical Industry Co., Ltd.) was used as reference material. The stationary value $(\Delta R)_s$ of the difference of thermister resistance ΔR was defined to be the value when the change of ΔR with time was nearly zero ($d\Delta R/dt \simeq 0$). The change was found to be less than 1.3×10^{-2} ohm/min. The value of $\lim_{c\to0}(\Delta R)_s/c$ was estimated from the intercept of the plot of $\Delta R/c$ *versus* concentration c at zero concentration.[7] The cryoscopic method using anthracene as a solvent was employed for the original pitch and the sublimation residue, which contained chloroform-insoluble components. The number-average molecular weights obtained will henceforth be referred to as mean molecular weight.

Instruments. Infrared spectra were measured with a Hitachi spectrometer (EPI-G3) by the usual KBr-disk method. Nuclear magnetic resonance spectra were obtained with a Hitachi spectrometer (R-24) using $CDCl_3$ as a solvent.

Results and Discussion

The temperature gradient curves of the sublimation furnace and each deposition zone are given in Fig. 1. Zones 1, 2, 3, 4, and 5 are numbered with decreasing temperature. Oily deposition product was obtained in the region between temperature 5 and room temperature, but the deposition was not sufficient for analysis. The relations between the yield of each fraction and heating temperatures of samples are given in Fig. 2. Sublimation yields tend to be constant at temperatures higher than 420 °C. However, the difference (indicated by □) has a tendency to increase with temperature. This indicates the possibility of degradation of the pitch at temperatures higher than 400 °C. As

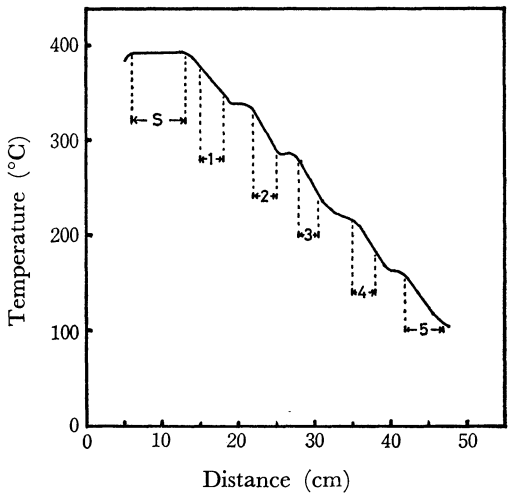

Fig. 1. Temperature gradient of sublimation furnace. S: sample, 1: 1st zone, 2: 2nd zone, 3: 3rd zone, 4: 4th zone, 5: 5th zone.

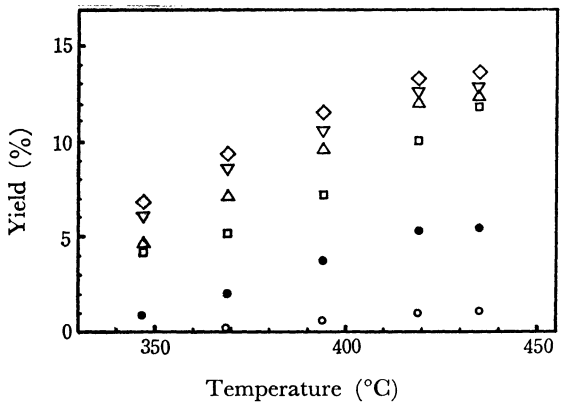

Fig. 2. Relations between yield of each zone and sample temperatures.
○: 1st zone, ●: 2nd zone, △: 3rd zone, ▽: 4th zone, ◇: 5th zone, □: difference between the sublimation yield of sample and the total of the yield of each zone from 1 to 5.

high an yield as possible is desirable, but degradation and/or reaction in pitch during sublimation should be avoided. The sublimation was therefore performed in the temperature range 390—395 °C, at a temperature lower than that of the preparation of the pitch (400 °C). The yields were 42—45%.

Sublimation of the mixture of the following eight compounds was performed: ovalene, violanthrene, decacyclene, coronene, 1,12-benzoperylene, perylene, pyrene, and anthracene. The results are given in Table 1. Each zone is divided into two parts, high temperature and low temperature except for zone 5. The high temperature side is similar to the low temperature side of the neighboring higher temperature zone. Results of elementary analysis of PVC pitch and mean molecular weights are given in Table 2. Mean molecular weights of sublimation products increase with rise in temperature of deposition zones. However, the mean molecular weight of the first zone is greater than that of the residue. This indicates the difference in structure of the main constituents.

NMR data are analyzed according to Brown *et al.*[8,9] and the results are given in Table 3. R denotes the number of condensed aromatic rings per average aromatic unit estimated from H_{aru}/C_{ar}. R′ values indicate actual numbers of aromatic rings per average aromatic unit obtained by the correction of R values with mean molecular weights and chemical formulas.

In the case of the unsubstituted aromatic hydrocarbons, vapor pressure and hydrogen content are usually lowered with increase in the number of rings, *i.e.*, with increase in molecular weight. The tendency is also observed with the aromatic compounds used in this work as seen from Table 1. In contrast, a considerable discrepancy from this trend is noted for PVC pitch fractions of zones 1 and 2.

The deposition of zone 1, though highest in molecular weight, exhibits higher H/C and smaller R than those of zones 2—4 as shown in Tables 2 and 3. It is

Table 1. Sublimation of polynuclear aromatic hydrocarbons

Zone number	Deposited hydrocarbons
2-H[a]	Violanthrene(A)[e]
2-L[b]	Ovalene, Decacyclene, Violanthrene(A)
3-H	Ovalene, Decacyclene
3-L	Ovalene, Violanthrene(B)[f]
4-H	Violanthrene(B)
4-L	Coronene
5-H	Coronene, 1,12-Benzoperylene
5-M[c]	Perylene, 1,12-Benzoperylene
5-L	Pyrene, Anthracene
6[d]	Pyrene, Anthracene

a) High temperature side. b) Low temperature side. c) Middle temperature region. d) Region between zone 5 and room temperature. e) Violanthrene A type. f) Violanthrene B type.

Table 2. Results of elementary analysis and mean molecular weights

Sample	Atomic ratio (H/C)	Molecular weight	Chemical formula
Zone 1	0.89	790	$C_{61}H_{54}$
Zone 2	0.81	600	$C_{47}H_{38}$
Zone 3	0.75	500	$C_{39}H_{29}$
Zone 4	0.76	440	$C_{34}H_{26}$
Zone 5	1.02	310	$C_{24}H_{24}$
Residue	0.60	730	$C_{58}H_{35}$
PVC pitch	0.83	570	$C_{44}H_{37}$

Table 3. Results of NMR measurements and NMR-derived parameters for each zone

Zone number	H_a/H_t	H_α/H_t	H_0/H_t	F_a	H_{aru}/C_{ar}	R	R′
1	0.39	0.32	0.30	0.72	0.68	4	3—4
2	0.40	0.32	0.29	0.75	0.61	5	3—5
3	0.38	0.34	0.28	0.77	0.54	6	6—8
4	0.37	0.34	0.30	0.76	0.54	6	6—7
5	0.36	0.31	0.32	0.67	0.76	2	2—4

H_a/H_t; Ratio of aromatic hydrogen(H_a) to the total hydrogen(H_t).
H_α/H_t; Ratio of hydrogen in saturated groups α to aromatic rings (H_α) to H_t.
H_0/H_t; Ratio of hydrogen on other saturated carbon atoms(H_0) to H_t.
F_a; Aromaticity defined as the ratio of the aromatic carbon to the total carbon.
H_{aru}/C_{ar}; The atomic hydrogen to carbon ratio of the hypothetical unsubstituted aromatic material.
R; Number of condensed aromatic rings per average aromatic unit estimated from H_{aru}/C_{ar}.
R′; Corrected value of R with mean molecular weight and chemical formula.

estimated that the average aromatic unit consists of 3—4 rings, corresponding to the unit weight of 180—220. The observed molecular weight indicates that the average molecule should contain about 4 aromatic units. Taking the chemical composition into account and allowing for the contribution of alkyl groups to the molecular weight, the average molecular structure may be described as a cluster of 3—4 aromatic units linked with aliphatic chains, each unit containing 3—4 condensed rings.

The fraction of zone 2 also shows an anomalous tendency exhibiting a smaller R than that of the fractions of zones 3 and 4 in spite of higher molecular weight. This suggests that the components of zones 1 and 2 are similar in chemical structure. The analysis shows that the average molecule consists of 2—3 aromatic units each having 3—5 fused rings on an average.

The results obtained with the fractions of zones 3 and 4 are almost the same except for molecular weight. Both fractions show lower H/C and H_{aru}/C_{ar} than those of other zones. Their molecular weights and chemical formula indicate that the average molecular structure can be described by the single aromatic unit, in contrast to the case of zones 1 and 2. The analysis shows that the average components of zones 3 and 4 are aromatic hydrocarbons containing 6—8 and 6—7 rings, respectively. NMR parameters and the molecular weights indicate that the aromatic compounds have alkyl substituents.

The deposition of zone 5 exhibits higher H/C and H_{aru}/C_{ar}, and lower F_a than those of other zones. It is estimated that the aromatic unit consists of 2—4 rings on an average. The mean molecular weight indicates that the average components are these aromatic units each having a few alkyl groups. It should be noted that the fraction is somewhat oily, which implies that it contains aliphatic compounds, since aromatic hydrocarbons with molecular weight near 300 are usually solid at room temperature.

The residue has the smallest H/C and as seen from the IR spectra (Fig. 3), the relative intensity of aromatic CH stretching (3060 cm^{-1}) to aliphatic CH stretching (2920 cm^{-1}) is the highest in all the fractions. It is thus inferred that the residue consists mainly of highly condensed aromatic compounds.

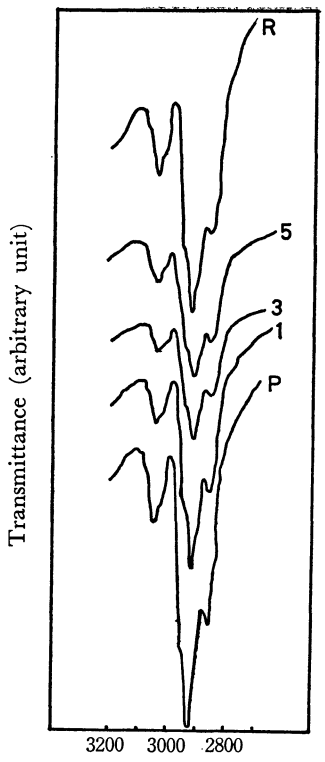

Fig. 3. IR spectra of PVC pitch, each zone and residue.
P: PVC pitch, 1: 1st zone, 3: 3rd zone, 5: 5th zone, R: sublimation residue.

References

1) J. D. Brooks and G. H. Tayler, *Carbon*, **3**, 185 (1965).
2) S. Otani, *Kogyo Kagaku Zasshi*, **61**, 447 (1958).
3) S. Otani, *ibid.*, **61**, 1324 (1958).
4) S. Otani and T. Ishikawa, *ibid.*, **65**, 1617 (1962).
5) S. Otani, *Carbon*, **3**, 31 (1965).
6) H. Marsh, J. W. Akitt, J. M. Hurley, J. Melvin and A. P. Warburton, *J. Appl. Chem. Biotechnol.*, **21**, 251 (1971).
7) "Kobunshisokuteiho," Jo, Baihukan Co., Ltd., Tokyo (1973), p. 57.
8) J. K. Brown, W. R. Ladner and N. Sheppard, *Fuel*, **39**, 79 (1960).
9) J. K. Brown and W. R. Ladner, *ibid.*, **39**, 87 (1960).