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AN EARLY STAGE CARBONIZATION PROCESS OF POLYVINYL CHLORIDE

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The cluster-like hydrocarbons characteristic of the pitch prepared from polyvinyl chloride at 400°C were not observed in the pitch prepared at 415°C. A reaction process in the early stage carbonization of the compound is proposed.

In a previous paper$^{1)}$ dealing with fractionation of pitch by vacuum sublimation, the presence of two types of hydrocarbons in the polyvinyl chloride pitch prepared at 400°C(PVC 400) was reported: one has a structure made up of a single aromatic compound with alkyl substituents and the other has a cluster-like structure composed of a number of aromatic unit linked together with aliphatic chains, each unit having three to five condensed rings. Otani has proposed that the latter form is typical for PVC pitch.$^{2)}$

As an extension of the previous study, investigations of PVC pitches prepared at different temperatures have been initiated. The present paper reports a preliminary result which shows a marked change in chemical structure of PVC pitch prepared at a higher temperature.

The apparatuses and procedures for vacuum sublimation, measurements of molecular weight and NMR spectra are essentially the same as those described previously.$^{1)}$ The sample was prepared by heating commercial polyvinyl chloride(Wako Pure Chem. Ind.) under nitrogen stream at 415°C for 5hr. The yield was 19.5%. The PVC pitch thus prepared (PVC 415) was observed to contain a small amount of mesophase as spherical droplets. The sublimation was performed by heating the sample at 405-410°C under evacuation by a rotary pump. The sublimation yields were 35-37%. The temperature gradient curve of the sublimation furnace is shown in Fig.1. Deposition zones are numbered from 1 to 5 in order of decreasing temperature.

The NMR data and parameters derived from the data according to Brown and Lander$^{3)}$ are given in Table 1. R denotes the average number of condensed rings per hypothetical aromatic unit estimated from H_{aru}/C_{ar}.

Number-average molecular weights and the results of elementary analyses are given in Table 2. Molecular weight of the fraction of zone 1 was not measured since the deposition was too scarce.

The observed molecular weights are reasonably explained by assuming that an average molecule in each of the fractions of zones 2-5 is composed of a single aromatic unit. The actual numbers of condensed rings R' per respective average molecule, obtained by the correction of R to explain these data consistently, are

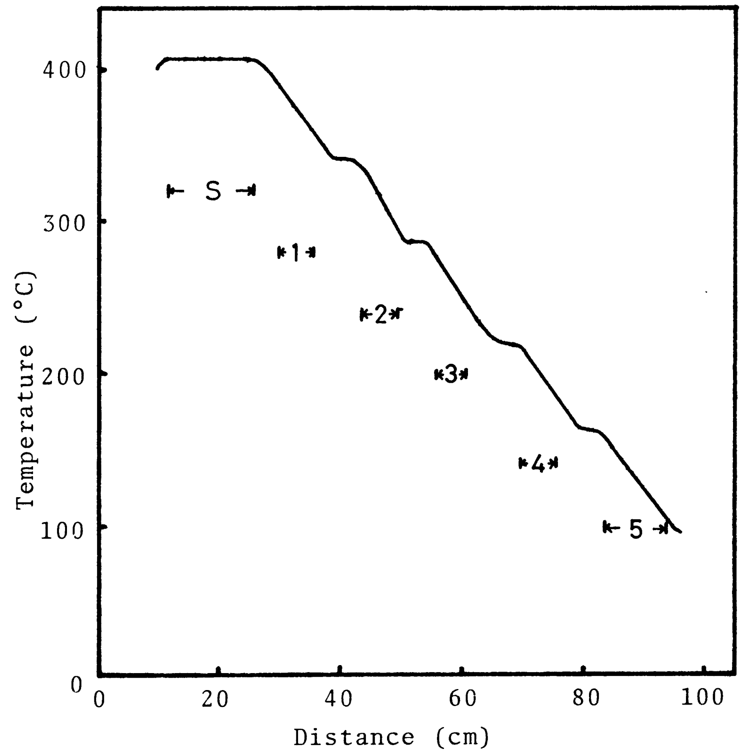

Fig.1. Temperature gradient of sublimation furnace.
S: sample, 1: 1st zone,
2: 2nd zone, 3: 3rd zone,
4: 4th zOne, 5: 5th zone,

Table 1. Results of NMR measurements and NMR-derived parameters for each zone

Zone number	H_a/H_t	H_α/H_t	H_o/H_t	F_a	H_{aru}/C_{ar}	R
1	0.38	0.36	0.26	0.78	0.52	8-9
2	0.42	0.35	0.23	0.79	0.53	8-9
3	0.43	0.34	0.24	0.78	0.58	6
4	0.41	0.34	0.25	0.76	0.60	6
5	0.40	0.32	0.28	0.76	0.58	6

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_o/H_t; Ratio of hydrogen on other saturated carbon atoms(H_o) 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 ; Numbers of condensed aromatic rings per average aromatic unit estimated from H_{aru}/C_{ar}.

Table 2. Results of elementary analysis and mean molecular weights

Sample	Atomic ratio (H/C)	Molecular weight	Chemical formula	R'
1	0.72			
2	0.70	610	$C_{48}H_{34}$	10-11
3	0.75	510	$C_{40}H_{30}$	7-9
4	0.79	390	$C_{30}H_{24}$	6
5	0.79	340	$C_{27}H_{21}$	5
Residue	0.56	800	$C_{64}H_{36}$	
PVC 415	0.69	580	$C_{46}H_{32}$	

Table 3. Sublimation of condensed aromatic hydrocarbons

Zone number	Deposited hydrocarbon
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 of the zone.
b) Low temperature side of the zone.
c) Middle temperature region of the zone.
d) Region between zone 5 and room temperature.
e) Violanthrene A type.
f) Violanthrene B type.

given in Table 2. Though the molecular weight of the fraction of zone 1 is not known, the atomic ratio and the NMR parameters similar to those of the fraction of zone 2 indicate that the two fractions are similar in chemical structure. The values of R' are in reasonable agreement with the numbers of condensed rings of the known aromatic hydrocarbons deposited at the respective zones under the same experimental conditions (Table 3).

A remarkable difference in chemical structure between the components of PVC 400 and PVC 415 is noted in that the cluster type hydrocarbons found with the fractions of zones 1 and 2 of PVC 400 are almost absent in PVC 415. This indicates that the cluster hydrocarbons characteristic of PVC 400 undergo degradation above 400°C.

From the results obtained for PVC 400 and PVC 415, it would be plausible to conclude that the formation of the cluster compounds occurs at temperatures below 400°C and at temperatures higher than about 400°C, the degradation of the clusters through scission of aliphatic linkage sets in accompanied by aromatic condensation.

Refferences

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