THE STRUCTURE AND PROPERTIES OF SOME PYROLYZED POLYMERS

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Pyrolytic conversion of polyvinylidene chloride to carbon proceeds to completion without significant loss of carbon as volatile compounds. The progress of carbonization was followed by reaction rate measurements and by changes in composition, X-ray scattering, d.c. resistivity and paramagnetic resonance absorption. Maximum unpaired electron concentration was exhibited by the composition, C_5HCl, but decreased beyond the limits of detection as the polymer coke approached the composition, $C_{10}HCl$. Over the same composition range d.c. resistivity decreased by a factor of 10^7 ohm cm and the electrical characteristics of the pyrolysates resembled p-type semiconductors. Correlations were observed between these results and similar studies of polyvinylchloride and preoxidized polyvinylbenzene pyrolyses.

Widespread adoption of ion-exchange resins in separation and purification processes has recently evoked the interesting suggestion[1] that useful absorbent carbons might likewise be derived from synthetic polymer sources. The scheme envisaged a series of carbon "molecular sieves" prepared by pyrolyzing homopolymers having monomer units of different shapes and sizes. Uniform carbon pore sizes would then be inherited from the regular structure of polymer predecessors. How this might be accomplished was uncertain because few valence angles and distances survive thermal decomposition unchanged[2]. Indeed, the present study of vinyl polymer pyrolysis indicates that original polymer configurations have only secondary importance. Instead, the actual course of carbonization is determined by the overall energy requirements for formation of rigid carbon materials[3].

All vinyl polymer molecules have skeletons of carbon chains or networks intermediate in structure between volatile organic compounds and graphite. During pyrolysis these carbon-carbon bond frameworks break into volatile fragments and/or condense to a dense mesh. Those which vaporize completely have been studied actively during the past decade[4]. Their decomposition conforms, by current concepts, to a three stage process consisting of chain scission, depropagation and termination. Monomer is regenerated from some polymers (i.e. polymethylmethacrylate[5]) by a zip reaction* which overcomes competing termination steps. More often such depolymerizations are blocked by side reactions involving hydrogen transfer.† Thus, hydrogen-rich polyethylene releases only a trace of monomer during vaporization. In fact, its predominant products have a molecular

[1] J. J. Kipling, Research **7**, 472 (1954)

[2] F. H. Winslow, W. O. Baker, N. R. Pape and W. Matreyek, J. Polymer Sci. **16**, 101 (1955).

[3] R. E. Franklin, Proc. Roy. Soc. (London) **209A,** 196 (1951).

[4] H. H. G. Jellinek, *Degradation of Vinyl Polymers*, Academic Press Inc., New York (1955).

[5] H. W. Melville, Science Progress **38,** 1 (1950).

* Reaction that moves rapidly along a polymer chain successively detaching or modifying monomer units.

† Free valences in highly reactive polymer radicals combine with hydrogens from elsewhere in the same radical structures or from adjacent polymer molecules, thereby interchanging hydrogens and radical sites.

weight distribution characteristic of that expected from a random cleavage process[6, 7]. In a few polymers, notably polydivinyl- and polytrivinylbenzene, hydrogen abstraction is sufficiently enhanced by extensive cross-linking[8] to cause some coke formation, though highest yields resulted from additional preoxidation or prechlorination treatments[2].

Carbonaceous residues from thermal decomposition of linear vinyl polymers have also been reported. The initial step in their conversion often consists of hydrogen elimination by the following general reaction,

$$-\begin{bmatrix} H & Y \\ C-C \\ H & X \end{bmatrix}_n \xrightarrow{\text{heat}} -\begin{bmatrix} H & Y \\ C=C \end{bmatrix}_n + HX$$
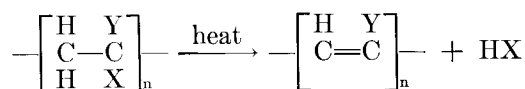
where X is chlorine in polyvinyl chloride[9, 10] and polyvinylidene chloride[10], acetate in polyvinyl acetate[11], hydroxyl in polyvinyl alcohol[12], etc. Most oxygen-containing polymers undergo additional side reactions involving scission of carbon-carbon bonds, for instance, acetaldehyde[13] and other gaseous carbon compounds are evolved from polyvinyl alcohol. The reactions of halogen-containing polymers are somewhat less complicated. Recently the distribution of pyrolytic products from the polymer series, $-(C_2H_4)_n-$, $-(C_2H_3F)_n-$, $-(C_2H_2F_2)_n-$, $-(C_2HF_3)_n-$,   and $-(C_2F_4)_n-$ was found to vary regularly with hydrogen-halogen ratios[14]. Both polymethylene and polytetrafluoroethylene vaporized completely by chain scission processes (random and zip type, respectively). But polyvinyl fluoride and polytrifluoroethylene, each having one HF per monomer unit, left small residues; while polyvinylidene fluoride, with two HF's per monomer unit, reduced to much larger yields of coke (30 % by weight of original polymer).

The high dissociation energies of C—F[15] and C—H bonds undoubtedly favor carbon-carbon bond scission reactions. On the other hand, replacement of fluorine by chlorine in some of the foregoing polymers lowers the energy needed for hydrogen halide elimination. Two of these chlorinated polymers, polyvinyl and polyvinylidene chloride, exhibit similar initial decomposition reactions but their carbon derivatives differ sharply in yield, density, structure and ease of graphitization. Detailed descriptions of the HCl evolution mechanism and the properties of the carbon products have been presented elsewhere[3, 9, 10]. This study concerns the important intermediate processes of carbon formation. Pyrolyses of polyvinyl chloride (I), polyvinylidene chloride (II), and preoxidized polydivinylbenzene (III) were followed gravimetrically and by X-ray analysis. In addition, paramagnetic resonance absorption measurements on pyrolysates of II and III[16] were correlated with changes in composition and d.c. resistivity.

PYROLYSIS KINETICS

Polyvinyl chloride was obtained from the B. F. Goodrich Co. in the form of a powder containing no inhibitor. Polyvinylidene chloride was prepared from distilled mono-

[6] S. L. Madorsky, Science **111,** 360 (1950).

[7] L. A. Wall, S. L. Madorsky, D. W. Brown, S. Straus and R. Simha, J. Am. Chem. Soc. **76,** 3430 (1954).

[8] F. H. Winslow and W. Matreyek (unpublished results).

[9] D. Druesedow and C. F. Gibbs, *Symposium on Polymer Degradation Mechanisms*, National Bureau of Standards Circular 525, 1953, p. 69.

[10] C. B. Havens, ibid., p. 107.

[11] N. Grassie, Trans Far. Soc. **48,** 379 (1952).

[12] E. H. Land and C. D. West, *Alexander's Colloid Chemistry*, Reinhold Publ. Corp., N. Y. (1946), v. 7, p. 178.

[13] P. D. Zemany, Anal. Chem. **24,** 1709 (1952).

[14] S. L. Madorsky, V. E. Hart, S. Straus and V. A. Sedlak, J. Research Natl. Bur. Standards **51,** 327 (1953).

[15] N. W. Luft, J. Chem. Phys. **23,** 973 (1955).

[16] F. H. Winslow, W. O. Baker and W. A. Yager, J. Am. Chem. Soc. **77,** 4751 (1955).

mer under nitrogen in sealed glass tubes heated to 40°C. The chlorine content of both polymers exceeded 99.5 % of the theoretical amount. Weighed samples (0.1–0.2 g.) were placed in thin-walled glass or quartz tubes ($\frac{3}{8}''$ in dia.), sealed with glass or mullite wool plugs and heated in nitrogen at atmospheric pressure. Variation of furnace temperature was ±1°C at 500°C and ±1.5°C at 800°C. Ambient temperature was measured with a thermocouple held within $\frac{1}{4}''$ of the sample. Weight loss was determined continuously during decomposition.

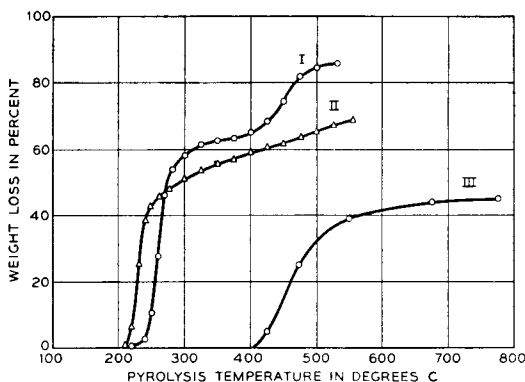Relative thermal stability of polymers I, II, and III are plotted in Figure 1. The

FIG. 1. Weight-loss characteristics of (I) polyvinyl chloride, (II) polyvinylidene chloride and (III) preoxidized polydivinylbenzene pyrolyzed by increasing temperature at the constant rate of 100°C per hour.
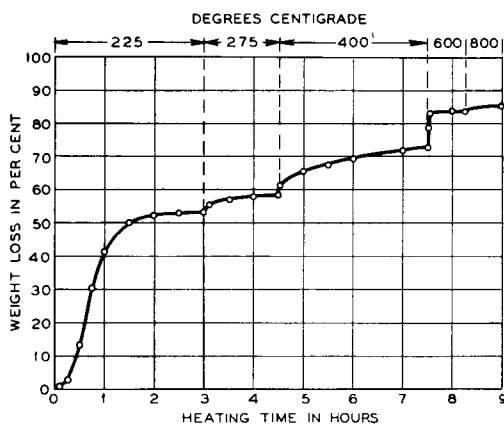
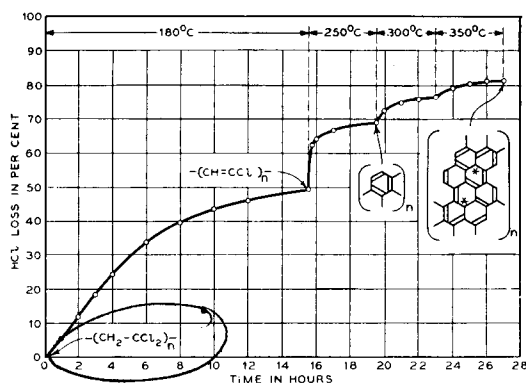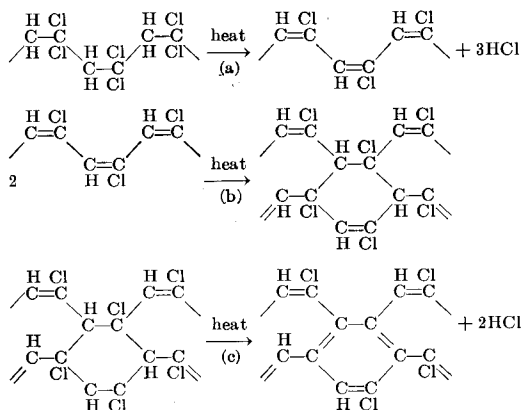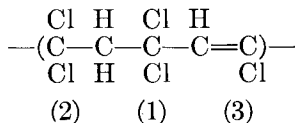FIG. 2. Stepwise pyrolysis of polyvinyl chloride

FIG. 3. Stepwise pyrolysis of polyvinylidene chloride. Probable valence structures at successive stages of heat treatment are represented schematically.

curves represent weight changes that occurred as sample temperatures were increased at the constant rate of 100°C per hour. Initial HCl evolution from I and II corresponded to a first order reaction. Two distinct volatilization processes are inferred by curve I and only one process by curve II. Careful selection of stepwise degradation temperature also reveals subtle condensation processes. Heating I (Figure 2) at 225°C for four hours caused a weight loss of 50 % or nearly 92 % of the initial chlorine content. Volatile carbon compounds were formed so readily above 400°C that only 15 % of the carbon in the original sample was left as residual coke at 800°C. Conversely, II (Figure 3) acted like a peculiar "carbohydrochloride" in converting quantitatively to carbon. Although half of its HCl was readily lost below 200°C, further liberation required progressively higher temperature until the process finally approached completion at 600°C.

Obvious hazards are inherent in any mechanistic interpretation of these pyrolyses that is based on classic organic chemistry. However, close qualitative agreement of the following hypothetical reactions with observed physico-chemical changes justifies a cautious synopsis.

$$\text{(a)} \quad \overset{\text{H Cl}}{\underset{\text{H Cl}}{\text{C--C}}}\ \overset{\text{H Cl}}{\underset{\text{H Cl}}{\text{C--C}}} \xrightarrow{\text{heat}} \quad \overset{\text{H Cl}}{\text{C=C}}\ \overset{\text{H Cl}}{\underset{\text{H Cl}}{\text{C=C}}} + 3HCl$$

$$\text{(b)} \quad 2\ \overset{\text{H Cl}}{\text{C=C}}\ \overset{\text{H Cl}}{\underset{\text{H Cl}}{\text{C=C}}} \xrightarrow{\text{heat}} \quad \overset{\text{H Cl}}{\text{C=C}}\ \overset{\text{H Cl}}{\text{C=C}}$$

$$\text{(c)} \quad \xrightarrow{\text{heat}} \quad + 2HCl$$

Both polymers I and II became colored at the very outset of degradation. The phenomenon has been attributed[17] to a zip reaction (equation a) that produces a linear polyacetylene (alternate single and double bonds) by successive release of adjacent HCl groups[9, 10, 18] along the polymer chain. The mechanism is consistent with the relative reactivities of three different types of C—Cl bonds[19]. For example, in a segment of an unsaturated II molecule the expected

$$\begin{array}{ccccc} \text{Cl} & \text{H} & \text{Cl} & \text{H} & \\ -(\text{C} & -\text{C} & -\text{C} & -\text{C} & =\text{C})- \\ \text{Cl} & \text{H} & \text{Cl} & & \text{Cl} \\ (2) & (1) & (3) & & \end{array}$$

ease of chlorine removal would be (1) allylic, > (2) paraffinic, > (3) vinyl. How HCl becomes detached is still undetermined. Grassie[11] concluded that dehydrohalogenation of I was like acetic acid loss from polyvinyl acetate which was allegedly a non-radical process.

Sudden loss of more HCl above 250°C as the residue from II sets to a rigid coke indicates onset of condensation. Of several possible mechanisms which have been

proposed[9] only the Diels-Alder reaction (equation b) fully satisfies the stepwise decomposition data. Each cyclic adduct has additional hydrogens and chlorines in highly reactive tertiary positions. These immediately split out (equation c) leaving thermally stable aromatic rings combined by polyene chains. Such condensation-dehalogenation sequences are known and are occasionally used in polycyclic aromatic hydrocarbon syntheses[20].

Cyclization in pyrolysis of I and II occurs primarily between adjacent polyene chains if the setting of drying oils is analogous[21]. Continued growth of fused ring regions might even be systematic since studies of α,ω-diphenyl polyenes[22] show that the terminal carbons attached directly to phenyl groups are preferred sites for such addition reactions. Conversely, steric hindrance imposed by network development should reduce or inhibit condensation[23a]. The final phase of ring fusion possibly leads to bridged ring systems[23b] and eventual removal of chlorine and hydrogen from bridge-heads or peripheral positions on graphite-like layer planes.

The advanced stages of I pyrolysis are quite complex. Cyclohexene adducts are only composed of carbon and hydrogen. Ordinarily, the high dissociation energy of C—H bonds favors alicyclic ring scission followed by escape of carbon and hydrogen as volatile compounds. But tertiary hydrogens attached to ring carbons are apparently vulnerable to transfer reactions[7] of the type found in reticulate hydrocarbon polymers[2]. Rapid removal of hydrogen above

[17] R. F. Boyer, J. Phys. and Colloid Chem. 51, 80 (1947).

[18] C. S. Marvel and E. C. Horning, Organic Chemistry, An Advanced Treatise, edited by H. Gilman, v. 1, 2nd ed., John Wiley and Sons, N. Y., 1943, p. 754.

[19] D. H. R. Barton and P. F. Onyon, J. Am. Chem. Soc. 72, 988 (1950).

[20] E. D. Bergmann, Research 4, 475 (1951).

[21] C. Boelhouwer, A. C. Jol and H. I. Waterman, Research 5, 336 (1952); C. Boelhouwer, W. A. Klaassen and H. I. Waterman, ibid., 7, S61 (1954).

[22] R. Kuhn and T. Wagner-Jauregg, Ber. 63, 2662 (1930).

[23] (a) K. Alder, chapt. on "The Diene Synthesis" in Newer Methods of Preparative Organic Chemistry, Interscience Publ. Inc., N. Y., 1948, p. 382; (b) ibid., p. 446.

400°C produces aromatic groups that rearrange to larger fused ring systems and volatile products like benzene[13]. Once established these aromatic regions probably act as thermally stable nuclei which then grow at the expense of surrounding aliphatic material.

Thus, I and II pyrolyses differ sharply in condensation processes. Thermally stable aromatic cross-links appear in II below 250°C but only develop in I above 400°C with the disappearance of most of the polyene-alicyclic structure. Hence, aromatic regions in I and to some extent those in III have more opportunity to reorder at least during the critical early stages in growth.

X-RAY ANALYSES

Evidence for the preceding mechanism proposals is fully corroborated by X-ray diffraction patterns representing various stages in the pyrolysis of polymers I (Figure 4) and II (Figure 5). Sample preparations are illustrated in Figures 2 and 6, re-
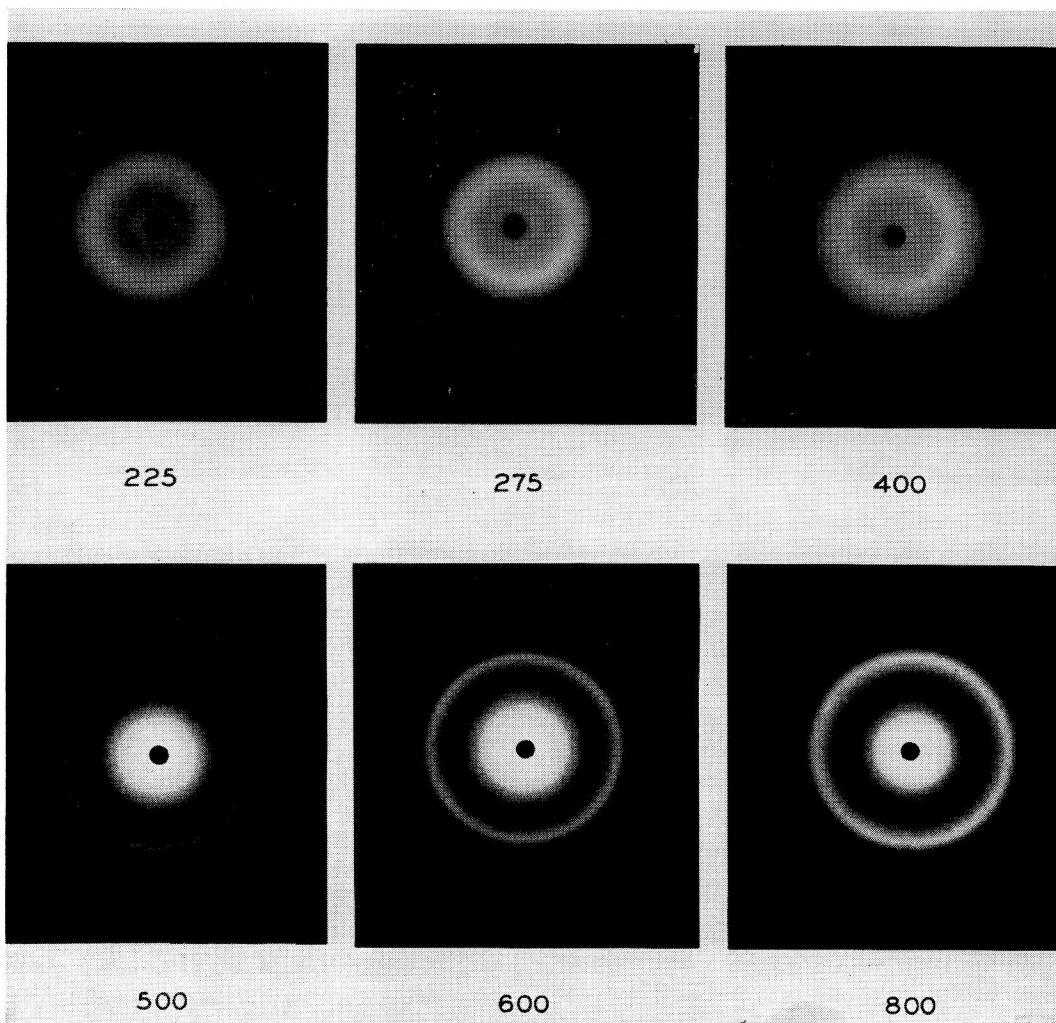

FIG. 4. X-ray patterns of polyvinyl chloride pyrolysis intermediates. Numbers signify maximum preparation temperature in degrees centigrade as shown in Fig. 2.
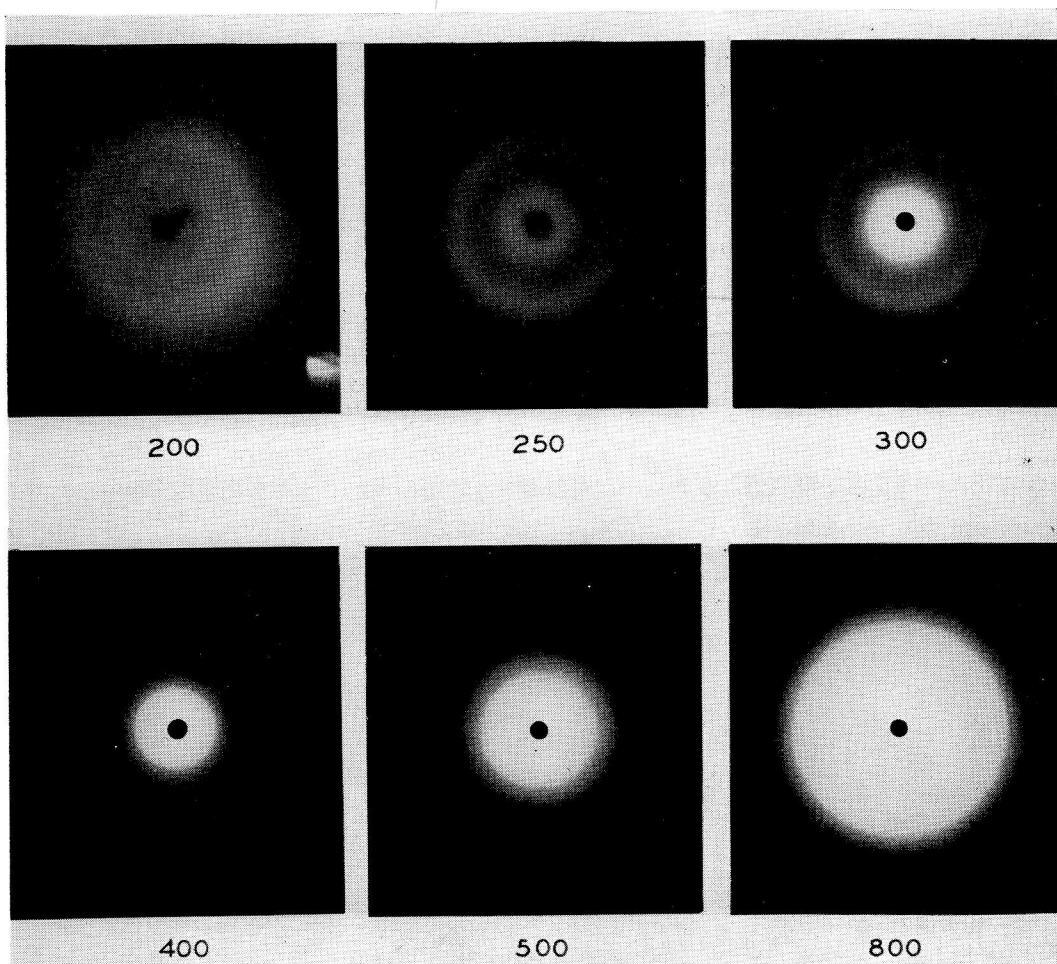
FIG. 5. X-ray patterns of samples representing successive stages in polyvinylidene chloride pyrolysis.

spectively. Numbers identifying individual x-ray diagrams signify maximum preparation temperatures of the corresponding samples. For example, diagram (400) in Figure 4 represents a pyrolysate obtained by heating I for 4 hours at 225°C, then 2 hours at 275°C and finally 3 hours at 400°C as shown in Figure 2. X-ray diagrams of I and II samples heat-treated at or below 300°C vaguely resemble diffraction patterns of cross-linked styrene polymers[2]. However, Figure 5 (400) is gas-like and succeeding diagrams (500 and 800), like hexachloro-

benzene carbons[24], show no tendency to reorder toward a graphite structure. Exposure times of the II x-ray pattern series varys directly with chlorine content from 240 hours for diagram (200) to 17 hours for diagram (800). The I series of diffraction patterns (exposure time, 16–24 hours) reflects an abrupt transformation between (400) and (500) that coincides with the second step in curve I, Figure 1. Diagram (400) is suggestive of a (275)–(500) composite and indicates the advent of graphite

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[24] J. Gibson, M. Holohan and H. L. Riley, J. Chem. Soc. 458 (1946).

layer formation that becomes the dominant (500) feature. These data fit the tentative hypothesis that II forms a compact homogeneous network of aromatic cross-links below 300°C, whereas polycyclic aromatic regions in I grow rapidly only above 400°C with relatively little encumbrance from tenuous aliphatic cross-bonds. At 500°C the aliphatic regions have almost entirely disappeared, partly by volatilization and partly by assimilation into the expanding multi-ring nuclei.

Still another coke series, intermediate in structure between I and II, was obtained (Figure 7) from III. Here, the original polymer already consisted of a dense network of phenylene groups interconnected by aliphatic chains. X-ray scattering from sample (600), Figure 8, was extremely diffuse, but patterns from succeeding samples (700), (800) and (1000) showed slight though definite signs of reordering.

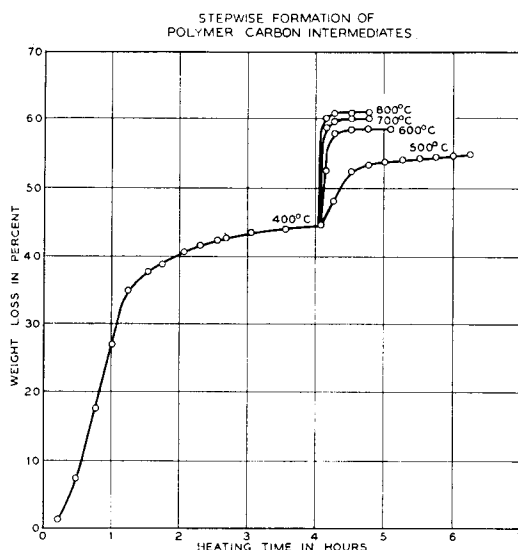STEPWISE FORMATION OF POLYMER CARBON INTERMEDIATES

FIG. 7. Procedure for preparation of preoxidized polydivinylbenzene pyrolysates whose structure is indicated by x-ray patterns in Fig. 8. [Reprinted with permission of the Editor, J. Polymer Sci. 16, 101 (1955).]

STEPWISE FORMATION OF POLYVINYLIDENE CHLORIDE PYROLYSIS INTERMEDIATES

FIG. 6. Conditions for formation of polyvinylidene chloride pyrolysis intermediates whose x-ray patterns are shown in Fig. 5.

ODD ELECTRONS, SEMICONDUCTIVITY AND COMPOSITION

Readjustments in bond distances and angles in polymer pyrolysates are accompanied by shifts in electronic distributions and mobilites. Diamagnetic susceptibilities of glucose and sucrose[25] chars were recently found to pass through minimum values at 650°C and 700°C, respectively. Other investigations[26, 27, 28] have demonstrated that unpaired electrons exist in many organic substances charred at temperatures below 700°C. Their presence in II and III derivatives have been detected by microwave resonance absorption techniques
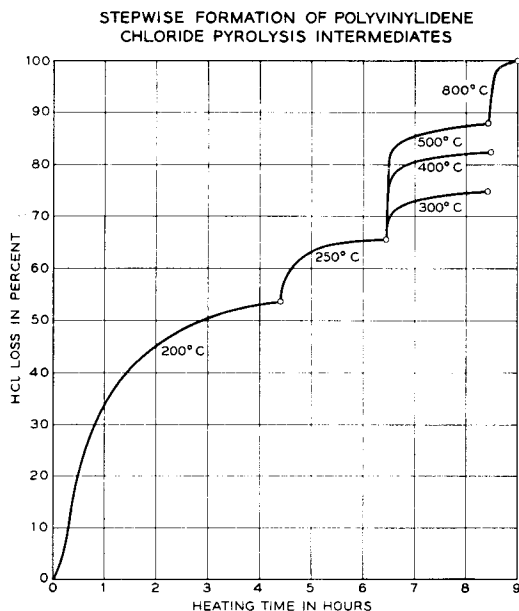
[25] V. A. Garten and D. E. Weiss, Aust. J. Chem. 8, 68 (1955).

[26] D. J. E. Ingram and J. G. Tapley, J. Chem. Phys. 23, 215 (1955).

[27] J. Ubersfeld, A. Etienne and J. Combrisson, Nature 174, 614 (1954).

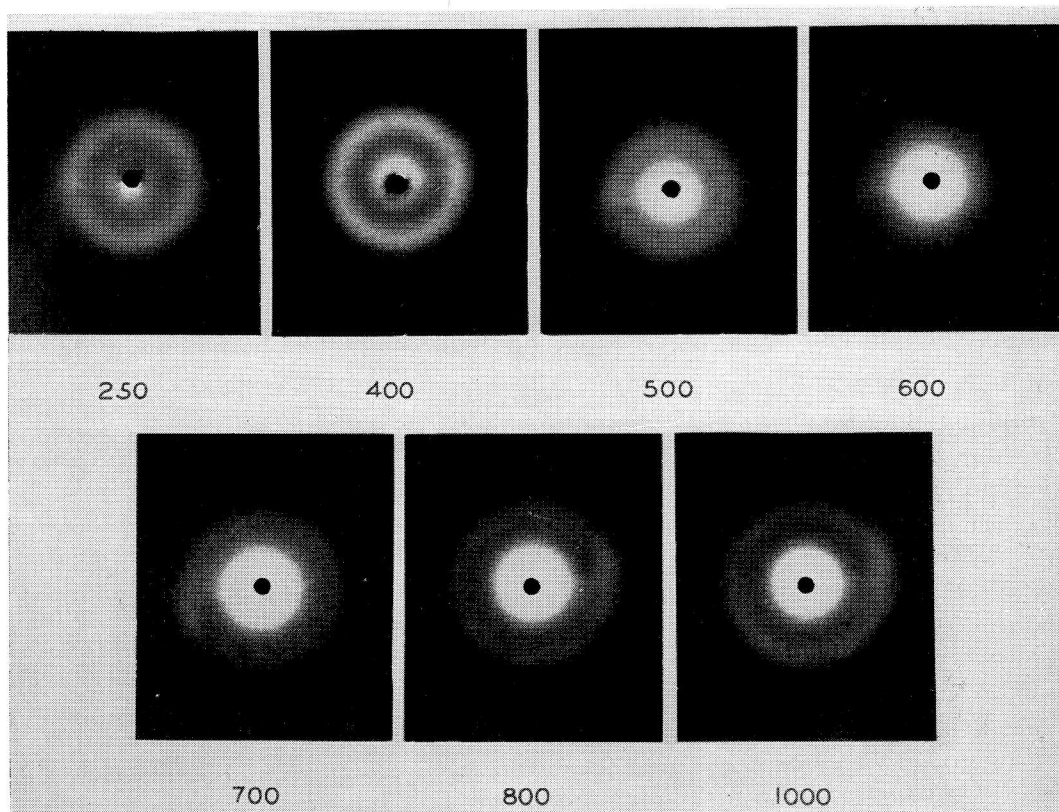[28] B. Commoner, J. Townsend and G. E. Pake, Nature 174, 689 (1954).

FIG. 8. X-ray scattering of preoxidized polydivinylbenzene pyrolysis intermediates. [Reprinted with permission of the Editor, J. Polymer Sci. **16**, 101 (1955).]

at room temperature in air[16]. The results are expressed in Figure 9 in terms of arbitrary units. Points on each curve represent maximum pyrolysis temperatures attained by heating samples according to the procedure outlined in Figure 1. One arbitrary unit equals approximately 3×10^{15} $(\Delta H)^2$ spins/cm³, where ΔH is the line width in oersteds between points of maximum slope of the absorption curve. Since ΔH ranged from 10 to 20 oe., the maximum odd electron concentration in both series of polymer cokes exceeded 10^{19}/cm³* and corresponded closely to empirical compositions of $(C_5HCl)_n$ for II (curve b) and $(C_5H_2)_n$ for III (curve a). Paramagnetic resonance absorption

diminishes rapidly with additional increase in carbon concentration in both series. It finally fades beyond the limits of detection at a carbon content of 80 % (atomic basis). Over the same range of composition (i.e. from $(C_5HCl)_n$ to $(C_{10}HCl)_n$) d.c. resistivity (figure 10) decreased by a factor of 10^7 ohm cm., and g-factors (Figure 11) declined steadily toward the free spin value.

During thermal breakdown of organic substances, unpaired electrons presumably occur as two general types[2], entrapped radicals (doublets) from severed σ bonds and resonance stabilized radicals (triplets) from ruptured π bonds. Without protection from the atmosphere, entrapped radicals are presumably transitory[29]. Yet, air exposure

* The granular samples had an apparent density of ~0.8.

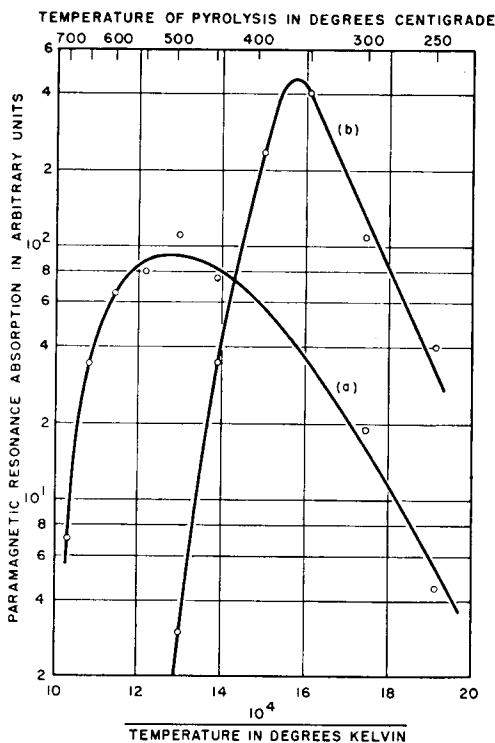[29] D. J. E. Ingram and J. G. Tapley, Chem. and Ind., 568 (1955).

FIG. 9. Dependence of paramagnetic resonance absorption on treatment temperature of (a) pre-oxidized polydivinylbenzene and (b) polyvinylidene chloride.
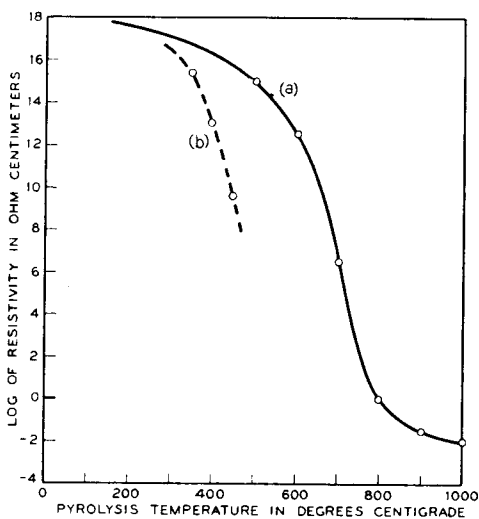

FIG. 10. Variation of d.c. resistivity with preparation temperature of (a) preoxidized polydivinylbenzene and (b) polyvinylidene chloride. [Reprinted with permission of the Editor, J. Am. Chem. Soc. 77, 4751 (1955).]
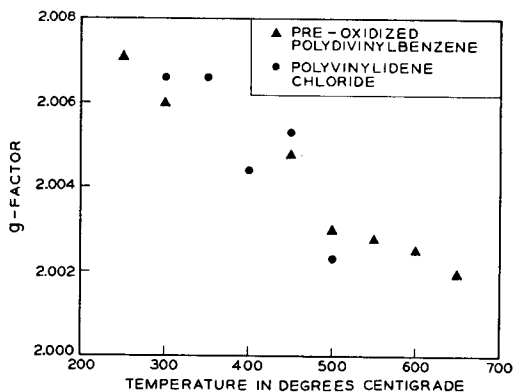

FIG. 11. g-factor of preoxidized polydivinylbenzene and polyvinylidene chloride residues as a function of preparation temperature. [Reprinted with permission of the Editor, J. Am. Chem. Soc. 77, 4751 (1955).]

over a two-year period caused negligible change in paramagnetic resonance absorption of II and III pyrolysates. Hence, odd electrons reside either in locations inaccessible to air and moisture or, more likely, in resonance stabilized configurations. Initial gain in their concentration is associated with a gradual rise in the number of isolated polynuclear aromatic systems. Maximum concentrations are reached as the expanding regions become contiguous and commence to coalesce. With further change, unpaired electrons become non-localized and vanish with the onset of semiconductivity. D.c. conductivity would therefore seem to depend primarily on orbital overlap between adjacent multi-ring regions of high resonance energy, whereas continuous conjugated paths between these regions are either ineffective or absent. This explanation is in accord with the views of Eley et al.[30] who attributed d.c. conductivity to π electrons and demonstrated that those in polycyclic aromatic systems are more effective than those in linear polyenes.

The g-values and evidence from supple-

[30] D. D. Eley, G. D. Parfitt, M. J. Perry and D. H. Taysum, Trans. Far. Soc. 49, 79 (1953); D. D. Eley and G. D. Parfitt, ibid, 51, 1529 (1955).

mentary sources like Hall effect[31], thermo-electric effect[32] and photoconductivity[33] measurements indicate that holes are majority carriers in organic substances containing less than 70 % carbon (atomic basis). Their origin and mode of movement are still obscure, but recent studies[16, 33] have led to the suggestion that absorption of heat or light by large polycyclic systems creates vast numbers[34] of current carriers through excitation of π electrons. Future elucidation of these mechanisms will have an important bearing on fundamental biological processes involving sight, respiration and growth.

[31] E. A. Kmetko, J. Chem. Phys. **21**, 2152 (1953).

[32] E. E. Loebner, Phys. Rev. **84**, 153 (1951), and Errata, S. Mrozowski, Phys. Rev. **86**, 1056 (1952).

[33] A. G. Chynoweth and W. G. Schneider, J. Chem. Phys. **22**, 1021 (1954).

[34] A. Many, E. Harnik and D. Gerlich, J. Chem. Phys. **23**, 1733 (1955).