Pyrolysis of Hydrocarbon Polymers

S. L. Madorsky

National Bureau of Standards, Washington, D. C.

In some recent work at the National Bureau of Standards, pyrolysis was carried out in a vacuum of about 10^{-6} mm Hg, and at temperatures ranging between 350° and 450° C, on polystyrene (*1*), polyisobutene, polyisoprene, polybutadiene, GR-S (25% styrene), and polyethylene (*2*). A sample of the polymer weighing about 50 mg was spread as a layer about 40 μ thick on a platinum tray and pyrolyzed in an evacuated Dewar-like apparatus by means of a platinum wire resistance furnace placed inside the apparatus. The products of pyrolysis were fractionated to facilitate analysis of composition by the mass spectrometer, or determination of the average molecular weight by a micromethod involving lowering of the freezing-point. The following fractions were obtained:

I. A solid residue, difficultly soluble in benzene or cyclohexane. No analysis was made of the composition or average molecular weight of this fraction, except in the case of polystyrene, where the average molecular weight was found to be of the order of 2000–2500.

II. A waxlike fraction volatile at the temperature of pyrolysis, but not volatile at room temperature. This fraction was quite soluble in benzene or cyclohexane and its average molecular weight was determined. No mass spectrometer analysis was made of this fraction.

IIIB. A liquid fraction volatile at room temperature but not volatile at – 75° C. No mass spectrometer analysis or molecular weight determination was made of this fraction. Its average molecular weight was estimated to be about 150 in all cases.

IIIA. A liquid fraction volatile at – 75° C. Mass spectrometer analysis of this fraction showed it to consist of the monomer and other compounds of a molecular weight less than that of the monomer or dimer. The average molecular weight could be calculated in this case from the data obtained in the mass spectrometer analysis.

IV. A gaseous fraction volatile at – 196° C. This fraction was analyzed in the mass spectrometer and was found to consist in all cases of CH_4.

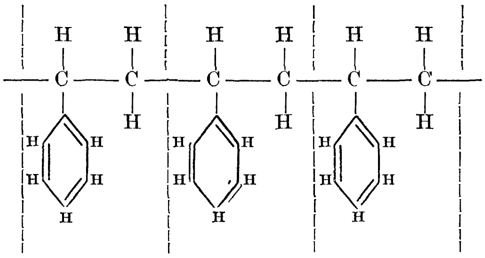
Within the temperature range specified, the relative amounts of the volatilized fractions and their average molecular weights for any polymer were found to be fairly constant, independent of temperature or extent of pyrolysis. The various fractions and their average molecular weights are shown in Table 1 for five polymers and one copolymer, GR-S. The data in this table can be used to calculate the number of ruptures of carbon to carbon links occurring in the macromolecular chain due to pyrolysis. In this calculation it is assumed that the polymer consists of one very long chain, and a double bond is counted like an ordinary C-C link.

Let Y_f be the yield of any given fraction in weight percent of the total volatilized part and M_f the average molecular weight of this fraction. Then the total number of molecules, small or large, which is the same as the total number of ruptures, P, per 100 g of a given polymer, is given by the expression

$$P = N\Sigma \frac{Y_f}{M_f}$$

where N is the Avogadro number.

The total number P_0 of C-C links in the macromolecular chain in 100 g of any polymer can be obtained by dividing the weight of the polymer by the average molecular weight per carbon in the chain and multiplying by N. Thus, for example, in the case of polystyrene



the average molecular weight per carbon in the chain is $104/2 = 52$, and the number of C-C links in 100 g is

$$P_0 = \frac{100 \times N}{52} = 1.923N$$

Ratio R of ruptured links P to original links P_0 can then be expressed in percent. Thus,

$$R = \frac{P \times 100}{P_0}$$

Table 2 shows values of P, P_0, and R for five polymers and one copolymer.

In the pyrolysis of hydrocarbons of ordinary molecular

TABLE 1

FRACTIONS OBTAINED IN THE PYROLYSIS OF SOME HYDROCARBON POLYMERS AND THEIR AVERAGE MOLECULAR WEIGHTS

Polymer	Waxlike II		Liquid IIIB		Liquid IIIA		Gas IV	
	%*	mol. wt	%*	mol. wt	%*	mol. wt	%*	mol. wt
Polystyrene	57.8	264	..	...	42.1	103.2†	.10	16
Polyisobutene	68.3	543	9.5	150	22.0	57.1	.22	16
Polyisoprene	88.7	577	5.6	150	5.7	68.5	.02	16
Polybutadiene	85.7	739	9.8	150	4.2	51.0	.30	16
GR-S	88.0	712	7.9	150	3.9	47.9	.19	16
Polyethylene	96.6	692	2.3	150	1.1	53.1	trace	16

* Percent of the total volatilized part.

† In the case of polystyrene, the fraction classed under II IA was collected at room temperature. Mass spectrometer analysis showed it to consist of 95 mole % styrene and 5 mole % toluene. There was no IIIB fraction from this polymer.

TABLE 2

PERCENT OF RUPTURED C-C LINKS IN THE TOTAL PYROLYZED PART*

Polymer	Original No. of links P_0	No. of ruptured links P	$R = \frac{P \times 100}{P_0}$ %
Polystyrene	1.923N†	.634N	33.0
Polyisobutene	3.572N	.588N	16.5
Polyisoprene	5.882N	.276N	4.7
Polybutadiene	7.407N	.283N	3.8
GR-S	6.061N	.270N	4.5
Polyethylene	7.143N	.175N	2.5

* Calculated for 100 g of the polymer.
† N = Avogadro's number.

size, decomposition does not take place until a temperature of about 800° C is reached. However, the introduction of a small amount of free radicals into the system induces the rupture of C-C links to take place at temperatures as low as 300° C (*3*). Since the hydrocarbon polymers discussed here decompose on heating at temperatures of 350°–450° C, it can be assumed that here too decomposition is due to the presence of free radicals.

TABLE 3

DISTRIBUTION OF C-C LINK RUPTURES BETWEEN SMALL AND LARGE MOLECULES*

Polymer	Monomeric type molecules		Intermediate and large molecules	
	Fraction IIIA	Fraction IV	Fraction IIIB	Fraction II
	%	%	%	%
Polystyrene	64.6	0.8	. . .	34.6
Polyisobutene	65.4	2.4	10.7	21.5
Polyisoprene	30.1	0.5	13.4	56.0
Polybutadiene	29.1	6.7	23.0	41.2
GR-S	30.1	4.5	19.7	45.7
Polyethylene	11.9	8.5	. . .	79.6

* Calculated in percent of total number of ruptures.

It is also assumed that the free radicals are the ends of the macromolecules, where rupture of C-C links to give molecules of monomer size may start. These free end radicals may in addition cause rupture of C-C links at some other points throughout the chain whenever they come up against these points at random.

Three mechanisms of chain rupture can be visualized:

1. Small fragments of monomeric size break away at the ends of a macromolecular chain until the residual fragment is small enough to escape into the gaseous phase at the temperature of pyrolysis. The products of pyrolysis will consist mainly of small-sized molecules.

2. The macromolecule breaks at random until fragments are sufficiently small to vaporize. In this mechanism the larger molecules, above the monomeric size, will predominate in the vaporized product.

3. A combination of mechanisms 1 and 2 giving rise to a mixture of small and large molecules, the ratio of the two groups of fragments depending on the polymer.

Table 3 shows the relative number of C-C ruptures due to monomeric type molecules (fractions IIIA and IV) as compared with the number of ruptures due to medium- and large-sized molecules (fractions IIIB and II), on the basis of $R = R_1 = 100$. It can be seen from this table that mechanism 1 predominates in the case of polystyrene and polyisobutene; mechanism 2 predominates in the case of polyethylene; and mechanism 3 in the case of the other polymers.

Some experiments carried out in this laboratory on the pyrolysis of polymethylmethacrylate at 400° C showed that about 90% of the C-C link ruptures were due to the formation of the monomer. This, then, represents a case where ruptures of C-C links occur almost exclusively at the ends of the macromolecular chains.

References

1. MADORSKY, S. L. and STRAUS, S. *J. Res. Nat. Bur. Stand.* 1948, **40**, 417; *Ind. eng. Chem.*, 1948, **40**, 848.
2. MADORSKY, S. L. *et al.* *J. Res. Nat. Bur. Stand.*, 1949, **42**, 499.
3. RICE, F. O. and RICE, K. K. *The aliphatic free radicals.* Baltimore: Johns Hopkins Press, 1935.

Di-(*p*-chlorophenyl)methylcarbinol, a New Miticide[1]

Oliver Grummitt[2]

Western Reserve University, Cleveland

In the course of a research program on synthetic organic insecticides related to 1,1-di-(*p*-chlorophenyl)-2,2,2-trichloroethane (DDT), the di-(*p*-halophenyl)alkylcarbinols $(p\text{-}XC_6H_4)_2C(OH)R$, showed high initial and residual toxicity to mites (*5*). This paper is a preliminary report on certain properties of this class of compounds.

Miticides have become indispensable since the widespread use of DDT. DDT is not only ineffective against this class of agricultural pests, but it also promotes the growth of mites by destroying predatory insects.

The di-(*p*-halophenyl)alkylcarbinols are unusual in the high specificity of their action. Although tests have been run against a wide variety of insects, only mites are affected at practical levels of concentration. Red spiders, European red mites, two-spotted mites, and Pacific mites can be controlled. There is no plant damage under ordinary spraying conditions. The mode of action has not been definitely established, but these compounds appear to be contact poisons.

Although exhaustive toxicity tests on laboratory animals have not been run, preliminary results with the di-(*p*-chlorophenyl)methylcarbinol on rats indicate acute and chronic toxicities which are not greater than DDT (*4*) and which subsequent study may show to be even lower. In the manufacture of pilot plant batches on a

---

[1] U. S. Patent 2,430,586, November 11, 1947, R. F. Ruthruff, Oliver Grummitt, and B. C. Dickinson, assigned to the Sherwin-Williams Company, Cleveland, Ohio.

[2] The writer wishes to acknowledge the financial support of the Sherwin-Williams Company, and the work of the following collaborators on the chemical phase of this study: A. A. Arters, R. E. Blank, Jean Fick, D. M. Marsh, and J. A. Stearns.