

## Laser Pyrolysis of Some Polymers in the Presence of Sodium Borohydride

YOSHIHIKO UEGAKI and TSUTOMU NAKAGAWA, *Industrial Products Research Institute, Shimomaruko, Otaku, Tokyo, Japan*

### Synopsis

The effect of sodium borohydride on laser pyrolysis of some polymers was investigated. It was observed that monomer yield was remarkably increased in the presence of sodium borohydride. The characteristic pyrogram was obtained under the conditions of low laser intensity and addition of sodium borohydride.

### INTRODUCTION

Recently, the usefulness of laser pyrolysis for gas-chromatographic analysis has been described especially for the characterization of polymer structures.<sup>1-8</sup>

The laser pyrolysis technique has the advantage that the entire event of laser energy absorption by the sample plume formation and quenching of the plume occurs in a time span much shorter than the fastest resistive heating method.<sup>1,3</sup> In laser pyrolysis it is most important to heat sample materials uniformly by laser beam and to obtain reproducible results. Recently, Vanderborgh<sup>7</sup> studied reproducibility of laser-induced pyrolysis by considering uniform thermal flux and reported that lasing on thin sections of material seems to lead to the most precise results. Wiley<sup>9</sup> and Ristau<sup>3</sup> pointed out that materials containing a small amount of hydrogen form large yields of acetylene. Ristau<sup>8</sup> discussed the relation of acetylene distribution in low molecular weight products to the hydrogen/carbon ratio of the samples from consideration of the plume quenching process and suggested the application of laser pyrolysis to elemental analysis.

Our previous work<sup>10</sup> on laser pyrolysis of aromatic carboxylic acids aimed at fixing and stabilizing the initial fragments or plume rapidly by the addition of a free-radical capture agent, e.g., sodium borohydride. It was found that sodium borohydride is effective for stabilization of phenyl radicals and characterization of the sample structure. In this work, we have investigated the effect of sodium borohydride for characterization of some polymers.

### EXPERIMENTAL

A detailed description of the laser gas-chromatographic instrumentation has been reported.<sup>11</sup> In brief, a normal mode pulse ruby laser was used to de-

grade samples contained in a quartz tube connected on-line to the inlet part of a Shimadzu-GC-4APF gas chromatograph, and products separation was made on a 5-m column packed with 8% dimethylsulfolane on 80/100 mesh Chromosorb P operated at 0°C for the low molecular weight hydrocarbon products and a 2-m column packed with 9% apiezon grease L on 80/100 mesh Chromosorb W operated at 150°C for the aromatic products.

The polymer samples used for this study are polyethylene (PE), polypropylene (PP), and polystyrene (PS). A small amount of powdered carbon (6 wt-%) was mixed with the sample material and, if required, sodium borohydride was uniformly added in half a sample monomer (unit number). A thin layer of the sample was coated on the sample support, and was set in the stream of the carrier gas. The sample was irradiated with a laser beam through a quartz window.

## RESULTS AND DISCUSSION

A sample mixed with carbon powder was degraded by a unfocused laser beam in a normal pulse mode (a, b, and c in Fig. 1). In the degradation of these polymers (PE, PP, and PS), their monomers and their unimolecular decomposition products are mainly formed. It is remarkable that acetylene is found in large yield. It has perhaps been formed by the unimolecular decomposition of monomer resulting from  $\beta$ -scission of initial free radicals. This decomposition is not useful for the elucidation of the original structures of polymers.

In previous work, it was found that sodium borohydride as a hydrogen donor is effective to fix and stabilize the initial fragments, especially phenyl radicals, produced by the decarboxylation of phenylcarboxylic acids. So we have tried to pyrolyze sample materials mixed with it. The data in Figure 1 show the fragmentation patterns resulting from the addition of sodium borohydride together with carbon powder (a', b', and c'). At first sight, it is found that the addition of sodium borohydride results in a significant increase in the yield of monomers, e.g., ethylene, propylene, and styrene from PE, PP, and PS, respectively. On the other hand, the yield of acetylene is remarkably decreased by its addition, and the hydrogenated monomers, e.g., propane and ethylbenzene, are formed in but low yield. Ethane could not be separated from ethylene in our gas chromatogram. An additional increment of sodium borohydride did not affect the product distribution in laser pyrolysis of aromatic carboxylic acids and fatty acid salts in our previous work. And also, in this work, the amount of sodium borohydride scarcely affected the pyrograms.

The variation of the individual products as a function of laser energy has also been investigated. It is important to note that the yield of the corresponding monomers decreased while the acetylene yield increased as a function of laser energy whether or not sodium borohydride is added. These trends are similar to that reported by Fanter<sup>5</sup> and Vanderborgh<sup>7</sup> on the laser pyrolysis of polystyrene. Therefore, it is obvious that laser output energy is necessarily low if characteristics of the parent structure are to be retained.

The following mechanism can be proposed to explain the reaction process and a role of sodium borohydride to account for the formation of the main pyrolysis products. As mentioned by Fanter,<sup>5</sup> the unimolecular decomposi-

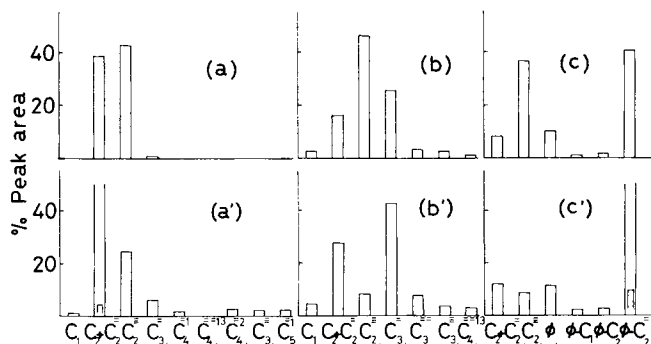
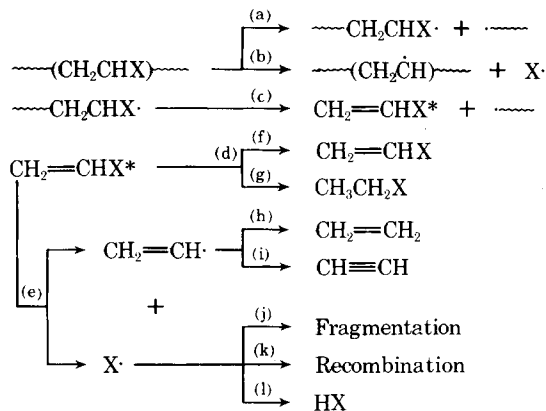


Fig. 1. Pyrolysis patterns of some polymers with (below) and without (above)  $\text{NaBH}_4$ .

Laser output: 0.1 joule. Samples: (a) polyethylene, (b) polypropylene, (c) polystyrene, Products:  $\text{C}_1$ , methane;  $\text{C}_2$ , ethane;  $\text{C}_2^-$ , ethylene;  $\text{C}_3^-$ , acetylene;  $\text{C}_3^-$ , propylene;  $\text{C}_3^=$ , allene;  $\text{C}_3^=$ , propine;  $\text{C}_4^=1$ , butene;  $\text{C}_4^=2$ , 2-butene;  $\text{C}_4^=-1,3$ , 1,3-butadiene;  $\text{C}_5^=1$ , 1-pentene;  $\phi$ , benzene;  $\phi\text{-C}_1$ , toluene;  $\phi\text{-C}_2$ , ethylbenzene;  $\phi\text{-C}_2^-$ , styrene.

tion of the polymer chain into two free radicals initiates the degradation of polyolefins, and then the radicals can dissociate to form fragments by  $\beta$ -scission as in laser pyrolysis of fatty acids.<sup>11</sup> The initial radicals are generated from main-chain cleavage (a) and/or by the elimination of branching groups (b). If only main-chain cleavage takes place, the degradation would proceed through process (c) because of deactivation of activated fragment  $\text{CH}_2\text{CHX}^*$  by sodium borohydride as reported in previous work.<sup>10</sup> So, the main products may be propane and propylene, styrene and ethyl benzene from PP and PS, respectively. But the experimental results suggest also that the initial degradation process takes place by the elimination of branching groups as well as from the cleavage of main chain. The bond dissociation energy of X from  $\text{CH}_2=\text{CHX}$  is 104, 90, and 101 kcal/mole for  $\text{X} = \text{H}$ ,  $\text{CH}_3$ , and  $\text{C}_6\text{H}_5$ , respectively. Ethylene radical  $\text{CH}_2=\text{CH}\cdot$  formed decomposes into acetylene and hydrogen with 39 kcal/mole.<sup>12</sup> So, if X is dissociated from  $\text{CH}_2=\text{CHX}$ , acetylene is immediately formed. An increase in laser energy more easily induces  $\beta$ -scission (c), hydrogen abstraction (i), fragmentation of monomer (e, j), and branching group elimination (b) (see Scheme 1). Then the yield of



Scheme 1. Possible schemes of the main mechanism of products distribution on laser pyrolysis.

monomer decreases and that of acetylene increases with an increment of laser energy. In the presence of sodium borohydride, the hydrogen radical is evolved from it by laser irradiation and it acts as a radical capture agent. So hydrogenation and deactivation of fragments are promoted and their dehydrogenation is prevented. But yields of hydrogenated products, e.g., propane and ethylbenzene, are little affected by the addition of sodium borohydride. Therefore, the quenching of monomer may take place more rapidly than their hydrogenation. In the presence of sodium borohydride, the formation of longer chain products than monomer is attributed to fixing large fragments formed through random scission of polymer chain.

### CONCLUSIONS

Pyrolysis patterns closely related to the original polymers are obtained by pyrolysis of polyethylene, polypropylene, and polystyrene with low laser output energy in the presence of sodium borohydride. The main products are monomer and products ( $\text{CH}_4$ ,  $\text{C}_6\text{H}_6$ ) formed by side chain cleavage.

### References

1. O. F. Folmer, Jr., and L. V. Azarraga, *J. Chromatogr. Sci.*, **7**, 665 (1969).
2. B. T. Guran, R. J. O'Brien, and D. H. Anderson, *Anal. Chem.*, **43**, 115 (1970).
3. W. T. Ristau and N. E. Vanderborgh, *Anal. Chem.*, **43**, 702 (1971).
4. O. F. Folmer, Jr., *Anal. Chem.*, **43**, 1057 (1971).
5. D. L. Fanter, R. L. Levy, and C. J. Wolf, *Anal. Chem.*, **44**, 43 (1972).
6. W. T. Ristau and N. E. Vanderborgh, *Anal. Chem.*, **44**, 359 (1972).
7. N. E. Vanderborgh and W. T. Ristau, *J. Chromatogr. Sci.*, **11**, 535 (1973).
8. N. E. Vanderborgh and W. T. Ristau, *Anal. Chem.*, **45**, 1529 (1973).
9. R. H. Wiley and P. Veeravagu, *J. Phys. Chem.*, **72**, 2417 (1968).
10. T. Kojima, F. Morishita, and Y. Uegaki, *Chemistry Letters*, Chemical Society of Japan, Tokyo, 1974, p. 1317.
11. T. Kojima and F. Morishita, *J. Chromatogr. Sci.*, **8**, 471 (1970); *Bunseki Kagaku*, **10**, 1303 (1971).
12. T. Kagiya, *Kinetic Research Method for Chemical Reaction*, Kagaku Dooin, Kyoto, 1970, p. 873.

Received August 12, 1975