

**Microstructure.** The third fruitful area for application of the P-GC technique is in obtaining information about polymer microstructure. Differences in molecular weight and distribution, stereoregularity, branching, cross-linking, or block structure can affect the kinetics and/or mechanism of the pyrolysis of homo- and copolymers (13, 16).

For example, true copolymers of ethylene and propylene can be distinguished from physical blends of the two materials. As shown above, a smooth curve was obtained for blends of various composition of the two commercial homopolymers. However, when a block copolymer of known (IR) composition was subjected to P-GC, the ethylene content was found to be about 30% too high, a figure well outside the experimental error. This behavior has also been found in other systems. In general, copolymers do not necessarily give the same proportions of decomposition products as do blends of the same composition (1).

The effects of major differences in stereoregularity and/or molecular weight on the pyrolysis products of polypropylene are illustrated in Figure 12. This system is currently undergoing further investigation. Differences between some straight chain hydrocarbons and a polymethylene and polyethylene of high molecular weight are shown in Figure 13. The regularity obvious in the pyrograms of the first three compounds is definitely perturbed in the commercial ethylene polymer. The perturbation may be due to chain branching, although data are insufficient at the present time to treat the system rigorously.

Pyrolysis-gas chromatography has already established itself as an excellent qualitative tool, and a useful quantitative instrument in selected cases. The indication that P-GC may prove useful for rapid microstructure elucidation should open new vistas to this technique as the procedures and equipment available gain in sophistication.

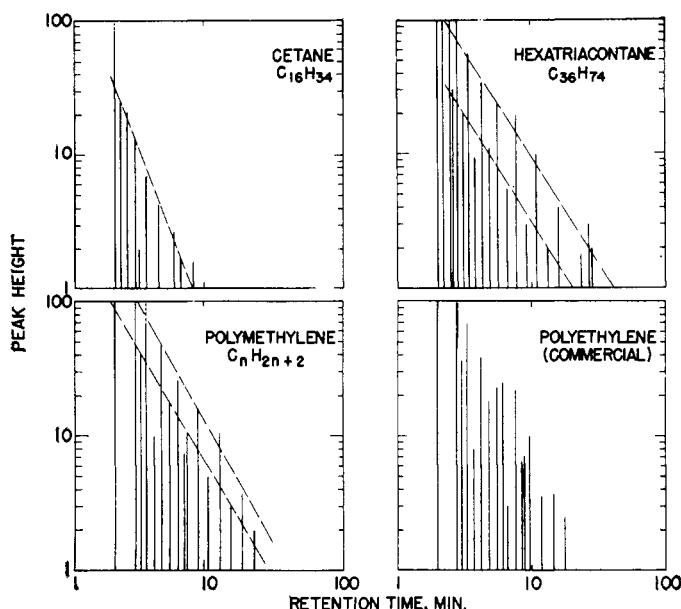


Figure 13. Hydrocarbon pyrolysis patterns, plotted on log-log scales

The regularity apparent in cetane, hexatriacontane, and polymethylene is absent in polyethylene

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#### Correction

### Theory of Stationary Electrode Polarography Single Scan and Cyclic Methods Applied to Reversible, Irreversible, and Kinetic Systems

In this article by R. S. Nicholson and Irving Shain [*ANAL. CHEM.* **36**, 706 (1964)] on page 722, Equation 87 should read as follows:

$$i = (nFAC_o^* \sqrt{Dk_f}) / \left[ 1 + \exp \frac{\alpha n_o F}{RT} (E - E^c + \frac{RT}{\alpha n_o F} \ln \frac{\sqrt{\pi D b}}{k_s} + \frac{RT}{\alpha n_o F} \ln \sqrt{\frac{k_f}{\pi a}}) \right] \quad (87)$$

Table I. Composition of Cellulose Esters<sup>a</sup>

Cellulose Propionate							
Wt. sample, mg.	0.50	0.75	1.00	1.00	1.00	1.25	Av.
Wt. % Propionate	89.0	88.8	89.8	88.6	90.3	90.4	89.5
Wt. % acetate	11.0	11.2	10.2	11.4	9.7	9.6	10.5
Cellulose Butyrate							
Wt. sample, mg.	0.75	1.00	1.25	2.00	Av.		
Wt. % acetate	29.9	29.1	29.4	29.1	29.4	} ± 0.5%	
Wt. % propionate	2.7	3.6	3.4	3.0	3.2		
Wt. % butyrate	67.4	67.3	67.2	67.9	67.4		

<sup>a</sup> Given as percentage of total ester content.