FREE RADICAL COPOLYMERIZATION OF ETHYLENE

Considerable importance has recently been attached (1) to a preprint-
ed preliminary report (2) from our laboratory in which the reactivity ra-
tios for the free-radical copolymerization of ethylene and propylene were
given as both being considerably greater than unity. This unlikely re-
sult was due to the inappropriate use of the Fineman-Ross method for
performing the calculation (3). Although the high r_2 value was retracted
in the oral report and omitted from final publication (4). the existence of
the preprinted values, which gave an r_1r_2 product of 10.2, has been used
as evidence that something unusual is occurring in ethylene copolymeri-
zation (1).

Therefore, it is appropriate to present additional data on ethylene—
olefin copolymerizations. The values given in Table I are closer to the
truth than the preprinted values, and were obtained using radioactive
monomers as previously described (4,5). The monomer in lower concen-
tration was always the tagged one.

TABLE I

Copolymerization Reactivity Ratios for Ethylene [a]

M_2	r_1	r_2
Propylene	3.2	< 0.62
Butene-1	3.2	< 0.64
Octene-1	3.2	not measured
Isobutylene	2.1	< 0.49
trans-Butene-2	7.5	not measured

[a] Ethylene = M_1 at 1020–1700 atm. and 130–220°C.

The r_2 values deserve special comment. These values are most accu-
rately determined at high M_2 (olefin) concentrations (3), but under these
conditions the molecular weights are so low that the copolymer equation
no longer holds (5). Being unsure as to how to make a valid correction,
we finally decided to apply the standard equation, which will give an r_2
value somewhat higher than the true value. We believe that the true r_2
values are not higher than given in Table I and not lower than one-half
of the tabled value. In this context, the r_1r_2 product is near unity for
these copolymerizations as it has been shown to be for other high pres-
sure ethylene copolymerizations (6). The recent claim to the contrary
(1) is probably the result of experimental difficulties such as were ex-

perienced in our laboratory in early work and is not supported by our recent data.

References

(1) Brown, F. E., and G. E. Ham, J. Polymer Sci., A2, 3623 (1964).

(2) Boghetich, L., G. A. Mortimer, and G. W. Daues, paper presented before Polymer Division, 141st National American Chemical Society Meeting, Washington, D. C., March, 1962; Polymer Preprints, 3, (1), 39 (1962).

(3) Tidwell, P. W., and G. A. Mortimer, J. Polymer Sci., A3, 369 (1965).

(4) Boghetich, L., G. A. Mortimer, and G. W. Daues, J. Polymer Sci., 61, 3 (1962).

(5) Mortimer, G. A., and L. C. Arnold, J. Polymer Sci., A2, 4247 (1964).

(6) Burkhart, R. D., and N. L. Zutty, J. Polymer Sci., A1, 1137 (1963).

George A. Mortimer

Plastics Division
Monsanto Company
Texas City, Texas