The Mechanism of the Copolymerization of Some Olefins with Maleic Anhydride*

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Alternating free-radical copolymerization have been explained as resulting from the polar interaction of a growing radical and a monomer,[1] from the stabilization of the transition state of propagation due to electron transfer,[2] and from the charge-transfer complex between monomers.[3]

Although ω-phenylalkenes copolymerize with maleic anhydride easily,[4] it has been found in this laboratory that 4-cyclohexyl-1-butene (CHBu) does not give a copolymer with maleic anhydride under the conditions under which 4-phenyl-1-butene copolymerizes. For example, the phenylbutene (1.0 mol./l.) and maleic anhydride (1.0 mol./l.) in methyl ethyl ketone, with azobisisobutyronitrile (0.25×10^{-2} mol./l.) as an initiator, gave 21% of a copolymer (M. W.> 2000) with an approximately 60 : 40 composition at 70°C in 5 hr. On the other hand, 4-cyclohexyl-1-butene and 1-octene gave trace amounts of solid products under the same conditions. This difference in reactivity cannot be considered to be due wholly to the different inductive effects of the benzene and cyclohexane rings, since these rings are separated from the double bond by two methylene groups.

Assuming similar initiation and termination

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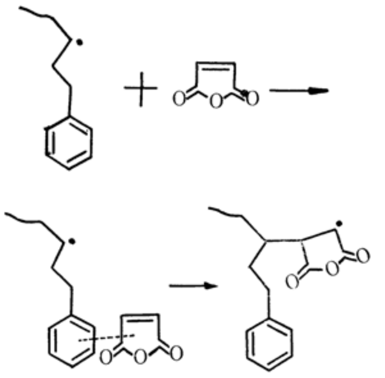
[1] C. C. Price, *J. Polymer Sci.*, **1**, 83 (1946).

[2] C. Walling, E. R. Briggs, K. B. Wolfstirn and F. R. Mayo, *J. Am. Chem. Soc.*, **70**, 1537 (1948).

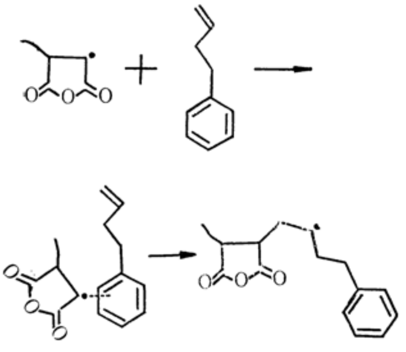
[3] S. Iwatsuki, Y. Tanaka and Y. Yamashita, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **67**, 1464 1467, 1470 (1964).

[4] M. M. Martin and N. P. Jensen, *J. Org. Chem.*, **27**, 1201 (1962).

reactions, the higher copolymerizability of 4-phenyl-1-butene may be attributable to the following propagation mechanisms, which are specific to this monomer:



(1)



(2)

In Eq. 1, the benzene ring of the propagating radical and maleic anhydride form a charge-transfer complex, while in Eq. 2 the propagating maleic anhydride radical forms a similar complex with the phenylbutene monomer.[5]

A third possibility to be considered is the intramolecular complex-formation of the phenylbutene radical, as may be assumed in the polymerization of vinyl benzoate.[6] The radical would then become a kind of ocnjugated free radical, and would show a very different reactivity from that of the cyclohexylbutene radical.

Which of these three schemes contributes most to the higher copolymerizability of the phenylbutene remains to be clarified. However, the process depicted by Eq. 2 seems important in the copolymerization of styrene and maleic anhydride; evidence which supports this mechanism has been presented elsewhere.[7]

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[5] M. M. Martin and G. J. Gleicher, *J. Am. Chem. Soc.*, **86**, 233 (1964).

[6] G. F. Santee, R. H. Marchessault, H. G. Clark and J. J. Kearny, *Makromol. Chem.*, **73**, 177 (1964).

[7] C. Aso, T. Kunitake and K. Watanabe, Papers presented at the 13th Discussion Meeting of the Society of High Polymers, Japan, November, 1964, p. 38.