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LETTER TO THE EDITOR

Proposed Participation of Excited Monomer in the Free Radical-Catalyzed High Pressure, High Temperature Polymerization of Ethylene

The polymerization of ethylene in the presence of oxygen and free radical initiators under conditions of high pressure and high temperature has been a commercially important process for many years. Although the reaction is usually carried out under conditions that are far from normal for a radical-catalyzed vinyl polymerization [1], it has generally been assumed that "chain initiation is probably identical to that in other vinyl polymerizations with typical peroxide and azo initiators" [2].

Ethylene polymerization under high pressure is generally initiated at temperatures of 100-200°C and reaches a peak temperature of 225-300°C or higher. The residence time in a commercial autoclave or tubular process is usually 20-120 sec. A source of free radicals is chosen that has a very short half-life, generally about 1 min, at the initiation temperature. In addition to single peroxides, mixtures of peroxides may be used where one peroxide has a 1-min half-life at the initiation temperature and the other peroxide has a 1-min half-life at the peak temperature [1].

The unusual use of "low temperature" catalysts at high temperatures and the high concentration of radicals generated per unit time as a result of the short half-life of the catalyst at the temperatures involved suggests the possibility of a radical-monomer interaction other than the usual addition reaction.

The polymerization of ethylene in the gas phase under high pressure at 30°C is initiated by UV light below about 3500 Å. The photopolymerization is strongly promoted by the presence of 100 ppm of oxygen although it is inhibited by a larger amount of oxygen [3, 4]. It has been suggested [4] that ethylene undergoes excitation to the triplet state by interaction with oxygen under irradiation. Polymerization is initiated either 1) by radicals arising from the decomposition of peroxides which result from the reaction of excited ethylene and oxygen, or 2) by direct addition of excited ethylene to unexcited ethylene monomer.

1015

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The polymerization of ethylene under high pressure at 40°C is readily initiated by γ radiation. However, the radicals produced by γ -rays do not react with ethylene in the absence of radiation. Irradiation with γ -rays or UV light is required for chain propagation [5]. It has been proposed that ethylene undergoes excitation and forms an excited dimer by reaction with ethylene in the ground state. Propagation involves the addition of the excited dimer to the growing chain radical.

It has recently been shown that chemically generated excited states may act as sensitizers for photochemical reactions [6, 7]. The thermal decomposition of an oxaoxetane [6] and oxidation of a diacyl hydrazide [6] and a diketooxaoxetane [7] have been shown to generate electronically excited states which can transfer their excitation energy to acceptors which subsequently undergo photochemical reactions.

The generation of excited states in the decomposition of organic peroxides and azo compounds has been demonstrated [8-11]. It may, therefore, be postulated that in the high pressure, high temperature polymerization of ethylene, the peroxides and other radical precursors decompose to excited species which transfer their excitation energy to ethylene monomer. The excited ethylene may react with ground state ethylene to initiate polymerization, possibly through the formation of an excited dimer which undergoes spontaneous polymerization. The excited dimer may also be involved in the propagation step, analogous to the proposed mechanism in the polymerization under gamma radiation [5].

The transfer of excitation energy from peroxide decomposition products has also been proposed in the copolymerization of conjugated dienes and maleic anhydride to alternating copolymers in which the unsaturation is rich in *cis*-1,4 structure [12, 13]. The copolymerization is initiated by peroxides as well as azo compounds at temperatures at which the catalyst has a half-life of 1 hr or less and the total reaction time is 0.5-1 hr. Decreasing the reaction temperature or the rate of catalyst addition results in increased yields of Diels-Alder adduct and decreased yields of copolymer. The proposed mechanism of polymerization involves a ground state diene-dienophile charge transfer complex which is readily converted to the cyclic adduct. The ground state complex becomes excited in the presence of the decomposing radical catalyst and the resultant excited complex undergoes polymerization.

The excited ethylene dimer may be similar to the excited charge transfer complex and exist predominantly in the dative form. The latter may undergo spontaneous initiation followed by conventional radical polymerization.

REFERENCES

- [1] K. W. Doak and A. Schrage, in *Crystalline Olefin Polymers*, Part I (R. A. V. Raff and K. W. Doak, eds.), Wiley, New York, 1965, p. 308.
- [2] P. Ehrlich and G. A. Mortimer, *Advan. Polym. Sci.*, **7**, 386 (1970).
- [3] S. Machi, M. Hagiwara, and T. Kagiya, *J. Polym. Sci., Part B*, **4**, 1019 (1966).
- [4] M. Hagiwara, H. Okamoto, T. Kagiya, and T. Kagiya, *J. Polym. Sci., Part A-1*, **8**, 3295 (1970).
- [5] M. Hagiwara, H. Okamoto, and T. Kagiya, *J. Polym. Sci., Part A-1*, **8**, 3303 (1970).
- [6] E. H. White, J. Wiecko, and D. F. Roswell, *J. Amer. Chem. Soc.*, **91**, 5194 (1969).
- [7] H. Güsten and E. F. Ullman, *Chem. Commun.*, **1970**, 28.
- [8] M. M. Rauhut, *Accounts Chem. Res.*, **2**, 80 (1969).
- [9] H. Fischer and J. Bargon, *Accounts Chem. Res.*, **2**, 110 (1969).
- [10] D. M. Hercules, *Accounts Chem. Res.*, **2**, 301 (1969).
- [11] R. E. Kellogg, *J. Amer. Chem. Soc.*, **91**, 5433 (1969).
- [12] N. G. Gaylord, M. Stolka, A. Takahashi, and S. Maiti, *J. Macromol. Sci.-Chem.*, **A5**, 867 (1971).
- [13] N. G. Gaylord, U.S. Patent 3,491,068 (Jan. 20, 1970).

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