Effects of Oxygen on the Polymerization of Ethylene over Supported Chromium Oxide Catalysts

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ABSTRACT: The polymerization of ethylene using as a catalyst chromium oxide supported on silica–alumina microspheres was studied first in the absence of oxygen and then with controlled amounts of oxygen (60–600 μmol/g of catalyst) present. Semibatch polymerization reactions were conducted at 135 and 185°F and at 160, 400, and 700 psig in a 2-l. autoclave with the catalyst suspended in cyclohexane, complete kinetic records being obtained by continuously monitoring the ethylene consumption rate with a mass flowmeter. In the absence of oxygen, the kinetics were characterized by an induction period that decreased with increasing temperature and pressure, followed by a period of essentially constant rate. In runs conducted in the presence of oxygen at 135°F, the induction period was greatly prolonged, the extent increasing with increased oxygen:catalyst ratio, but substantial polymerization activity always developed whenever sufficient time was allowed. However, the runs at 185°F produced little activity even after 30 hr. These data and the appearance of carbonyl-containing compounds in the diluent after a successful polymerization in the presence of oxygen indicate that the inhibiting effect of oxygen involved the adsorption or chemisorption of an oxygenated hydrocarbon species onto the catalyst.

When ethylene is polymerized using a catalyst of chromium oxide on silica–alumina microspheres suspended in an organic diluent at temperatures below approximately 110°, the polymer forms directly as a solid on and in the catalyst particles. As a result, the catalyst is repeatedly fractured and active surface reexposed to the monomer. If the reaction is conducted in a semibatch manner at constant temperature and pressure (*i.e.*, ethylene is fed "on demand" to maintain the desired pressure, and the product is allowed to accumulate within the reactor), then the polymerization rate increases during an induction period from zero to some level where it remains essentially constant for an extended period. Both the duration of the induction period and the magnitude of the constant rate depend on the reaction temperature and pressure, the amount of catalyst used, and the quantity of catalyst poisons present.[2-4]

Though there is much disagreement concerning the chemical nature of the active sites in this catalyst system, it is well accepted that they but thinly populate the catalyst surface. Fully activated catalysts containing the usual 1.0–2.5% Cr are thought to possess only 0.30–30.0 μmol of sites/g of material.[5-9] With such a low concentration of polymerization centers, it is not surprising that catalyst poisons are a matter of some concern. Oxygen, an omnipresent impurity in monomer and diluent alike, has long been recognized[10-12] as a potent inhibitor of polymerization activity, and a number of investigators have studied this phenomenon.[3,7,13-15] Despite these efforts, however, the mechanism of oxygen poisoning under the semibatch conditions described above is still unclear because some studies[7,15] were conducted in the absence of a diluent and others[3,13] were limited to reports of average rates of polymerization (yield/duration of run). Adding to the uncertainty is the fact that, while one group[14] observed product molecular weight to be independent of oxygen concentration, another[15] found it to steadily decrease as the oxygen level was increased.

The present study was undertaken as an attempt to provide additional insight into the nature of oxygen poisoning by revealing the effects of oxygen concentration on both the induction and constant rate phases of the reaction. Toward this end, two series of semibatch polymerizations were run in a 2-l. autoclave using cyclohexane as the diluent, one in the absence of oxygen and the other with controlled amounts of oxygen, ranging from 60 to 600 μmol per g of catalyst, admitted in the diluent. The first series determined the oxygen-free reaction rate all through the induction period and at the constant level for temperatures of 135 and 185°F and ethylene pressures of 160, 400, and 700 psig. In the second series, the effects of various levels of oxygen concentration were studied at the highest of the above pressures and at both temperatures. Products were characterized by DSC thermogram, molecular weight distribution, and infrared spectrum.

Experimental Section

Catalyst Preparation. Approximately 1 kg of silica–alumina (87–13) microspheres[16] was suspended in a 0.55 *M* solution of chromic acid. After 30 min of vigorous agitation, the slurry was filtered, and the cake was removed to an oven where it was dried for 4 hr at 95–115°. The resulting finely divided, bright yellow material was then stored under dry nitrogen.

Prior to each run, a weighed portion drawn from the above store was placed in a Pyrex ampoule and heated under vacuum for 8 hr. During the last 5 hr, the furnace temperature was 550°, and the residual pressure in the ampoule was approximately 10^{-2} mm. At the end of the heating period, the ampoule was sealed, still under vacuum, and mounted in the reactor. Catalyst prepared in this manner contained 4.07% Cr, 96.5% of which was Cr(VI).

Diluent Preparation. Phillips Pure Grade cyclohexane was further purified by repeated passage through columns of BASF

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(2) Yu. I. Yermakov, G. K. Boreskov, V. A. Dzis'ko, and L. I. Ivanova, *Dokl. Phys. Chem.*, 143, 289 (1962).

(3) Yu. I. Yermakov and L. P. Ivanov, *Kinet. Catal. (USSR)*, 6, 804 (1965).

(4) Yu. I. Yermakov, G. K. Boreskov, M. G. Slin'ko, and V. B. Skomorokhov, *Kinet. Catal. (USSR)*, 6, 821 (1965).

(5) P. B. Ayscough, C. Eden, and H. Steiner, *J. Catal.* 4, 278 (1965).

(6) A. Guyot, J.-C. Daniel, M. Durrieu, and M. Ptack, *J. Polym. Sci., Part A*, 3, 1765 (1965).

(7) C. Eden, H. Feilchenfeld, and Y. Haas, *J. Catal.*, 11, 263 (1968).

(8) J. P. Hogan, *J. Polym. Sci., Part A-1*, 8, 2637 (1970).

(9) V. A. Zakharov and Yu. I. Yermakov, *J. Polym. Sci., Part A-1*, 9, 3129 (1971).

(10) J. P. Hogan and R. L. Banks (to Phillips Petroleum Co.), U. S. Patent 2,825,721 (March 4, 1958).

(11) A. Clark and J. P. Hogan in "Polythene," A. Renfrew and P. Morgan, Ed., Interscience, New York, N. Y., 1960, pp 29–34.

(12) J. P. Hogan in "Copolymerization," G. E. Ham, Ed., Interscience, New York, N. Y., 1964, pp 89–113.

(13) G. K Boreskov, V. A. Dzis'ko, and T. Ya. Tyulikova, *Dokl. Phys. Chem.*, 136, 9 (1961).

(14) B. G. Fedotov, A. S. Semenova, M. I. Leitman, N. M. Korobova, N. B. Kashirima, and L. G. Stefanovich, *Sov. Plast.*, **No. 10**, 12 (1968).

(15) Yu. I. Yermakov, L. P. Ivanov, and A. I. Gel'bshtein, *Kinet. Catal. (USSR)*, 10, 333 (1969).

(16) Davison Chemical F-1-13 Cracking Catalyst.

R-311 catalyst and Linde 3A molecular sieves until no oxygen or water could be detected in samples therefrom. Details of the glc analyses employed are available elsewhere,[17] but we note here that the practical detection limits were about 1 ppm (by weight) for oxygen and 5-10 ppm (by weight) for water. A large batch of diluent was purified to something below these levels and used for all of the "oxygen-free" runs by pressure transferring the desired charge for each run through a smaller vessel of calibrated volume in a procedure which precluded the readmission of atmospheric contaminants. In the later runs, where controlled amounts of oxygen were to be admitted to the reaction system *via* the diluent, the charge for each run was reoxygenated to the desired level (while in the smaller vessel) by bubbling it with a prepurified and dried gas mixture of 2% oxygen and 98% nitrogen.

Polymerization. A schematic diagram of the experimental system is shown in Figure 1. The reactor was a 2-l., stainless steel, Magnedrive Packless autoclave,[18] equipped with electrical heating jacket, variable-speed magnetically driven turbine impeller, cooling coils, baffles, thermowell, pressure gauge (0–1000 psi), dip tube for inlet and sampling, and vapor phase outlet for vent and purging. For improved temperature control, bare thermocouples were employed, one between the reactor wall and the heating jacket and one entering the reactor through a Conax seal and immersed directly in the reaction mixture. In this way the temperature of the reactor contents during polymerization was normally controllable to within ±1-2°F.

Upon assembling the reactor with the catalyst ampoule affixed to the impeller, the vessel was heated to 400°F and thoroughly purged with nitrogen that had been deoxygenated and dried by passage through columns of BASF R-311 catalyst and Linde 3A molecular sieves. When the analysis train, consisting of a Lockwood-McLorie Model GP trace oxygen analyzer and an Engelhard-Chemie Technik Aquanal moisture monitor, indicated that the oxygen and water levels in the effluent purge gas had fallen below 0.5 and 1 ppm, respectively, the reactor was considered "clean," and the nitrogen purge was replaced with similarly purified ethylene. The diluent was then charged and allowed to equilibrate with ethylene at the pressure and temperature for that run. Actuating the impeller then shattered the catalyst ampoule and started the run, which was continued until either the constant rate period was definitely established or the accumulation of polymer within the reactor made temperature measurement and/or control impossible. Throughout the course of the run, a Matheson Model H-20-K mass flow transducer (and associated recorder) monitored the flow of ethylene to the reactor, and, since polymerization was conducted at constant temperature and pressure, this gave a direct and continous measure of reaction rate.

Differential Scanning Calorimetry. DSC thermograms were recorded on a Perkin-Elmer instrument, the Model 1 B, using a sample size of 2–5 mg and a heating rate of 5°/min.

Gel Permeation Chromatography. Molecular weight distributions were determined from elution curves obtained on a Waters Model 200 gel permeation chromatograph equipped with a four column (10^7, 10^6, 10^4, and 10^3 Å) system having a plate count of 730 plates/ft. Measurements were made in 1,2,4-trichlorobenzene at 135° using a sample concentration of 0.5 mg/ml. Calibration (molecular size *vs.* retention time) was accomplished with a set of Waters polystyrene standards. All samples were drawn from fully homogenized yields, *i.e.*, the entire yield for a given run was comminuted and thoroughly mixed prior to being sampled.

Infrared Spectroscopy. Infrared spectra of polymer yields and reaction diluents were recorded on a Perkin-Elmer Model 257 grating infrared spectrophotometer. Films of whole polymer samples were obtained by pressing 100- to 200-mg portions between Teflon sheets at 190° and 10,000 psig. Films of low molecular weight extracts, however, were prepared by allowing the polymer to slowly melt to a thin sheet between two salt plates.

Results

Polymerization in the Absence of Oxygen. The rate data for this series of runs are shown in Table I and in Figures 2 and 3. The curves in the latter are compressed versions of the mass flowmeter recordings, obtained by dividing the original chart into segments and plotting the average rate for each segment against its midpoint time. As was expected, these curves showed that all runs contained a constant rate period preceded by an induction period during which the rate was first immeasurably small and then steadily increasing. In most cases, the duration of the induction period was determined by inspection of the compressed curve, and the magnitude of the constant rate by time averaging the original strip-chart record over the segment posterior to this. In C-17, however, the last 40 min were not included in the latter computation since, during that period, the ethylene supply was too low to maintain the initial reactor pressure. The validity of using mass flowmeter records as the measure of rate of polymerization was confirmed by the agreement between calculated and observed yields (see last two columns of Table I). The overall soundness of the experimental technique was verified by the reproducibility of the data when duplicate experiments were run (in Table I, compare C-7 and C-3 and C-17 with C-12).

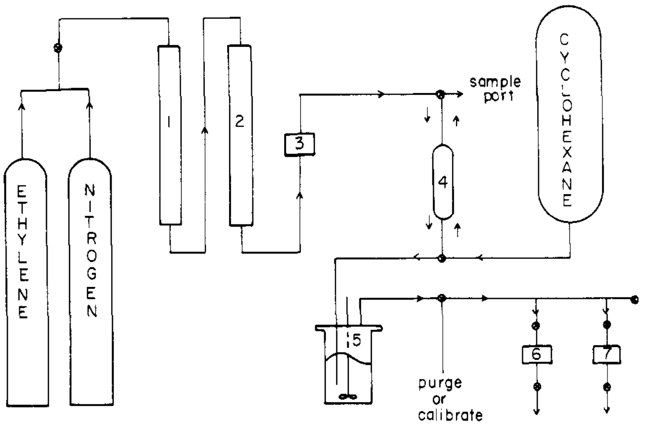

Figure 1. Schematic diagram of polymerization system: (1) column packed with BASF R-311 catalyst; (2) column packed with Linde 3A molecular sieves. (3) mass flow transducer; (4) calibrated volume vessel; (5) reactor; (6) oxygen analyzer; (7) moisture analyzer.

It is evident from both the curves and the tabulated data that the magnitude of the constant rate increased with increasing reaction temperature and pressure. The steepness of the increase with pressure was somewhat unexpected in view of earlier work[19,20] that showed a leveling off in the rate *vs.* pressure curve between 450 and 750 psig. It is possible, however, that this apparent discrepancy is due to differences in experimental technique. The previous investigators did not continuously monitor rate, as was done in this study. but instead only determined the total accumulation of polymer at the end of a 1-hr period. Thus, it is not unlikely, especially in view of the high yields they report, that the leveling off occurred not because the surface rate of reaction became independent of pressure but because during these runs polymer accumulated to such an extent that the rate became mass transfer controlled. To illustrate this reasoning more clearly, two hypothetical 1-hr runs will be considered: one conducted at 400 psig and the other at 700 psig. In the first, after steadily increasing over the initial 10 min to 300 g/hr, rate remains constant for 40 min and then falls rapidly to about 30 g/hr. In the second, a steady rate of 450 g/hr is reached in about 6 min, but this level is maintained for only 24 min before it rapidly decays to about 45 g/hr. Total accumulation is approximately the same in the two runs, but the rate–time pattern in each is different and clearly pressure dependent.

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(17) V. G. Murphy, Ph.D. Thesis, University of Massachusetts, 1971.

(18) Manufactured by Autoclave Engineers, Inc., Erie, Pa.

(19) A. Clark and G. C. Bailey, *J. Catal.*, 2, 230 (1963).

(20) A. Clark and G. C. Bailey, *J. Catal.*, 2, 241 (1963).

Table I
Polymerization in the Absence of Oxygen

Run	Reaction Temp (°F)	Reaction Pressure (psig)	Catal Charge (g)	C_6H_{12} Charge (g)	Duration of Run (min)	Induction[a] Time (min)	Constant[b] Rate (std cm^3/g per min)	Calcd[c] Yield (g)	Actual[d] Yield (g)
C-4	135	160	3.310	860	190	110	93	54	63
C-11	135	400	3.379	860	180	60	224	131	148
C-16	135	700	1.696	860	125	80	704	165	155
C-7	185	160	3.375	860	100	55	199	66	72
C-3	195	155	3.302	860	125	70	186		
C-17	185	370-55[e]	1.692	860	105	30	535	92	101
C-12	185	400	3.383	860	75	23	502		
C-30	185	700	0.682	860	65	5	1390	97	116

[a] Determined by inspection of the curves in Figures 2 and 3. [b] Obtained by time averaging the original strip-chart record over the entire constant rate period, the onset of the latter being determined by inspection of the curves in Figures 2 and 3. [c] Obtained from total areas under original strip-chart records. [d] Weight of polymer recovered from reactor. [e] Supply pressure too low to maintain constant pressure in reactor.

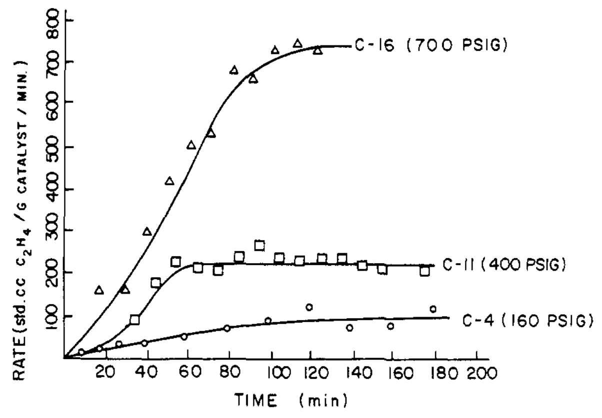

Figure 2. Specific rate of polymerization *vs.* time for oxygen-free runs at 135°F.

If this uncertainty concerning the interpretation of the earlier data is warranted, then the present findings may have some theoretical significance, since the previous investigators used their results as evidence of a propagation mechanism in which the polymer chain grows by addition of adsorbed, rather than free, monomer. Other evidence based on molecular weight data was also presented, but it was later shown[21] that, when chain transfer with monomer is a significant mode of chain termination, no distinction between the two propagation mechanisms can be made on the basis of molecular weight considerations. Thus, while the data of the present study are too few to be conclusive, they do support the contention[21] that propagation proceeds *via* the addition of free monomer.

The effects of reaction temperature and pressure on the length of the induction period were more expected. With but one exception, C-16, the induction time decreased when either temperature or pressure was increased. These trends are in agreement with observations of Yermakov and Ivanov[3] and are consistent with a mechanism[22] in which the catalyst particles initially charged to the reactor are continuously fractured, thereby exposing new active sites, until some critical particle size is reached, whereupon there is no further reduction in size and hence no further increase in the number of active sites. Within this scheme, an increase in temperature or pressure hastens the attainment of the critical particle size (shortens induction) by increasing the rate of polymer growth which, in turn, increases the rate of catalyst fracture. The unexpectedly long induction period for C-16 may have been caused by the accidental (and undetected) admission of a small quantity of air. This possibility is treated further below.

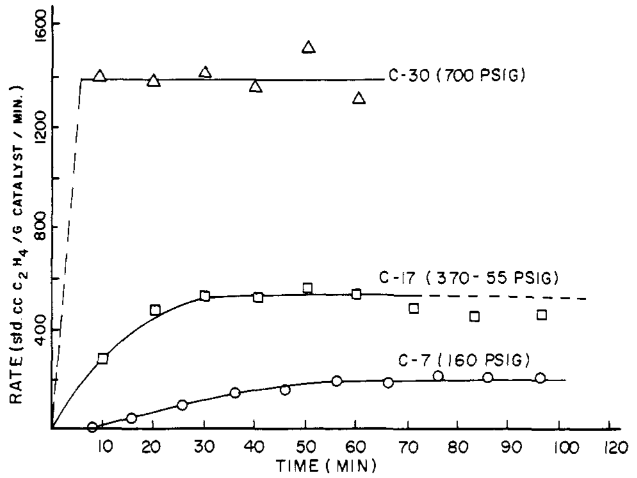

Figure 3. Specific rate of polymerization *vs.* time for oxygen-free runs at 185°F.

Polymerization in the Presence of Oxygen. The rate data for this series are presented in Table II and in Figure 4. As in the preceding series, the rate curves were obtained from the mass flowmeter records. Even a cursory inspection of these plots reveals that the presence of oxygen greatly lengthened the duration of the induction period. In fact, in no case was the onset of a constant rate period observed since the accumulation of large amounts of polymer with attendant loss of temperature control invariably forced termination of the run while the rate was still rising. The rate curve for O-14 did seem to be leveling off just before shutdown, but it is unlikely that the reaction was kinetically controlled, for by that time over 300 g of polymer had accumulated within the reactor. The degree to which the induction period was affected clearly increased as the oxygen catalyst ratio, R (μmole/g), was increased. In O-8, with $R \approx 60$, polymerization commenced immediately and reached a high, though still increasing level within 1 hr; but in O-9 and O-10, with $R \approx 200$, measurable activity did not occur until well into the second hour; and in O-12 and O-14, with $R \approx 350$, more than 12 hr passed before reaction was observable. The magnitude of the effect for $R > 300$ was not expected; consequently, in a few cases (O-6 and O-7) experiments were terminated prematurely, and in another (O-12) some in-

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(21) A. Guyot, *J. Catal.*, 3, 390 (1964).
(22) H. L. Whitaker and G. B. Wills, *J. Appl. Polym. Sci.*, 13, 1921 (1969).

Table II
Polymerization in the Presence of Oxygen

Run[a]	Reaction Temp (°F)	Catal Charge (g)	C_6H_{12} Charge (g)	O_2:Catal Ratio (μmol/g)	Duration of Run (hr)	Yield (g)
O-6	135	1.939	760	600	2	Trace
O-7	135	3.483	775	310	9	Trace
O-8[b]	135	3.488	580	60	1.25	145
O-9[c]	135	1.761	645	235	4	205
O-10[c]	135	0.883	590	190	8	215
O-12[d]	135	0.888	800	345	22	280
O-14[c]	135	0.731	700	375	27	325
O-15	185	0.771	700	250	7	Trace
O-16[e]	185	0.765	705	190	31	45

[a] All runs were at 700 psig. [b] Rapid reaction took place immediately, reaching 520–600 std cm^3 of C_2H_4/g of catalyst per min, when loss of temperature control forced a shutdown. [c] See Figure 4. [d] There was no apparent reaction for 12 hr, but over 200 g of polymer formed between 12 and 19 hr; no record was obtained, however, since the operator was not present; observation of still ongoing reaction between 19 and 22 hr indicated only a very low rate, probably due to heavy accumulation of product. [e] There was no indication of reaction for 24 hr and only a slight indication thereafter.

Table III
Polymer Characterization

Run	Reaction Temp (°F)	Reaction Pressure (psig)	O_2:Catal Ratio (μmol/g)	Melting[a] Range (°C)	Peak[a] Temp (°C)	No.-Av[b] Mol Wt (g/g-mol)	Wt-Av[b] Mol Wt (g/g mol)	Dispersity[c] Index	Rate of Polym[d] at Shutdown (std cm^3/g per min)
C-4	135	160		128–141	138	36,100	370,000	10.2	93
C-11	135	400		129–142	139	31,800	515,000	16.2	224
C-16	135	700		130–142	139	42,500	750,000	17.6	704
C-7	185	160		128–140	137	26,100	281,000	10.8	199
C-17	185	400		127–139	135	24,500	384,000	15.7	535
C-30	185	700		127–139	136	17,700	390,000	22.0	1390
O-9	135	700	235	130–142	139				870
O-10	135	700	190	128–142	139	20,900	556,000	26.5	1250
O-12	135	700	345	129–141	137				
O-14	135	700	375	128–140	135	52,700	882,000	16.7	475
O-16	185	700	190	126–139	135	45,200	559,000	12.4	100[e]

[a] From DSC analyses of particulate yield only. [b] From GPC analyses of homogenized yield. [c] Weight-average molecular weight/number-average molecular weight. [d] Units are std cm^3 of C_2H_4/g of catalyst per min. [e] Maximum estimate; mass flowmeter not accurate at this level.

formation was lost due to a failure of faith after a prolonged period of unrewarded diligence.

The most striking aspect of the above results is that, in all runs at 135°F, a significant rate of polymerization developed whenever sufficient time was allowed. Indeed, in O-9 and O-10, the level of activity just prior to termination was even higher than that observed in C-16 in the supposed absence of oxygen.[23] Thus it is evident that the polymerization sites were only temporarily inactivated, rather than permanently destroyed, by the presence of oxygen. Although these data alone cannot determine the mechanism of inhibition, it seems likely that oxidation products of cyclohexane or the remnants of oxygen terminated polymers are involved. The length of time required for regeneration of activity, however, does strongly imply that the interaction between the active sites and the inhibiting species, whatever its identity, is stronger than mere physical adsorption. The reason for the lack of recovery of activity in the two runs at 185°F is not clear, but it may be related to a reported[7,24] strengthening of the coordination between Cr and oxygenated hydrocarbons as temperature is increased.

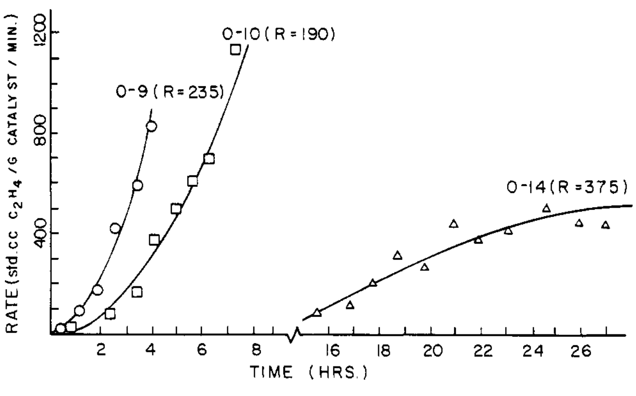

Figure 4. Specific rate of polymerization *vs.* time for runs in the presence of oxygen. *R* = oxygen:catalyst ratio (μmole/g). All runs at 135°F and 700 psig.

Polymer Characterization. Melting ranges and melting peak temperatures for polymers from both phases of the study are given in Table III. These data were obtained from DSC thermograms of samples drawn only from the fine, granular portions of the yields. In several runs, however, the product also contained a considerable quantity of aggregated material, *i.e.*, polymer which had been swollen or even dissolved during its residence in the reactor. Since this only occurred in runs at 185°F (C-7, C-17, C-30) or in runs in which the yield was unusually high (O-12

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(23) In retrospect it seems likely that a trace quantity of air was inadvertently introduced into the reactor during C-16 and that the rate was not at its full potential at shutdown. What was originally thought to be the onset of the constant rate period probably reflects the competition between the rate-enhancing effect of catalyst renewal and the rate-retarding effect of polymer accumulation.

and O-14), it was attributed to local heating in poorly mixed zones of the reactor which, it was reasoned, would have the complimentary effects of increasing the solvating power of the diluent and decreasing the molecular weight of the polymer produced. When aggregated material was incorporated in the DSC sample, the thermogram departed from the base line at a temperature 4-5° lower, and two overlapping peaks appeared. Evidently, then, this material possessed a less perfect crystal structure than the pristine polymer. In this regard it is interesting that the same result was reported earlier in the case of Ziegler-Natta polyethylene by Wunderlich[25] and by Ingram and Schindler.[26]

To determine whether the presence of oxygen during polymerization had any effect on the chain length of the polymer produced, molecular weight distributions were obtained by gel permeation chromatography (GPC). The results of these analyses are presented in Table III, and a sample distribution curve is shown in Figure 5. In comparing O-14 with C-16 and O-16 with C-30 it is clear that in these cases there was a strong increase in molecular weight as the oxygen:catalyst ratio was increased. A comparison of O-10 with C-16 would at first appear to indicate the opposite effect, but in O-10 the high final reaction rate and the large accumulation of polymer strongly suggest that there was local overheating within the reaction mass late in the run. This would cause a decrease in molecular weight for that period and would be reflected in the GPC results because of the homogenized total sampling procedure used. The fact that the dispersity index (M_w/M_n) for O-10 is so large (26.5 as opposed to 17.6 for C-16 and 16.7 for O-14) can be viewed as a further indication of thermal effects in this run. Significant too in this regard is that in C-30, which developed the greatest specific reaction rate, the molecular weight was relatively low and the dispersity index relatively large.

If the above interpretation is correct, the presence of oxygen causes not only a decrease in the time average rate of polymerization (owing to a prolongation of the induction period) but also an increase in the molecular weight of the product. It follows, therefore, that if oxygen inhibits polymerization by terminating growing polymer chains it cannot be released when dead polymer is displaced and polymerization renewed, for in that event a monotonic decrease in molecular weight would be observed with increasing oxygen:catalyst ratio. In addition, it may be concluded that a reduction in the number of active sites leads to an increase in the ratio of chain propagation to chain transfer at those sites still functioning. This latter result is consistent with the work of Clark[27] in which M_n was observed to increase as the surface concentration of Cr in the catalyst preparation was reduced.

At least one author[28] has claimed to have observed carbonyl stretching bands in the ir spectrum of polyethylene produced in the presence of oxygen. Since this would be strong evidence for the chain termination mode of deactivation, similar results were sought in this study. Unfortunately, however, spectra obtained for whole polymer samples from the yields of the O series were devoid of any absorptions characteristic of oxygen linkages. To test the possibility that oxygen containing groups were just too few to be seen in the whole polymer, spectra were also obtained for low molecular weight fractions of this series isolated by extraction with boiling 1-butanol. These contained several bands that were unresolved in the previous scans, but they did not differ significantly from the spectra recorded for control samples isolated from the polymer produced in the C series.

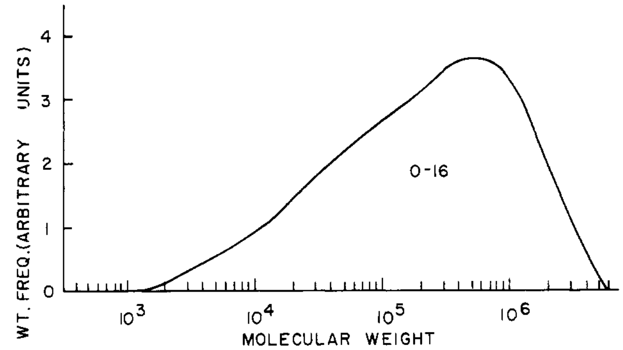

Figure 5. Molecular weight distribution of polymer produced in O-16. M_n = 45,200. M_w = 559,000.

A much more profitable experiment, as it turned out, was to record the ir spectrum of the diluent after a run. Unfortunately, this was discovered too late for an exhaustive study, and only the diluents remaining from O-3, O-5, O-6, O-14, and O-15 were available for such testing. Significantly, however, only in the case of O-14, the one run in the group in which polymerization occurred, was any difference from the reference liquid, Phillips Pure Grade cyclohexane, detected. Equally important, this difference involved the appearance of a band in the carbonyl stretching region. This was interpreted to mean that regeneration of a catalyst poisoned by exposure to oxygen involves the displacement of a carbonyl compound of relatively low molecular weight from the catalyst surface. Others[29] have reported that ethylene is readily oxidized to formaldehyde by supported chromium trioxide according to the reaction

$$\mathrm{Cr(VI)} + \mathrm{C_2H_4} \rightarrow \mathrm{Cr(II)} + 2\mathrm{CH_2O}$$

which does not involve molecular oxygen. The same workers also noted, however, that the formaldehyde remains bound to the support until displaced by water; consequently, this reaction would not seem relevant to the present findings.

Discussions and Conclusions

The polymerization of ethylene over supported chromium oxide catalysts was studied in both the absence and the presence of molecular oxygen. In the former experiments a steep rise in the magnitude of the constant rate with increasing pressure was noted, indicating a propagation mechanism in which growth occurs by the addition of free, as opposed to adsorbed, monomer.

At 135°F, the presence of oxygen was found to greatly prolong the duration of the induction period, the magnitude of the effect increasing as the oxygen:catalyst ratio was increased. It is emphasized, however, that significant polymerization activity always developed when sufficient time was allowed, implying that the effect of oxygen was reversible at this temperature. Since a substantial period of time was required for activity to reappear and carbonyl stretching bands were observed in the ir spectrum of the diluent when it did, it seems likely that this inhibition involves the temporary chemisorption of a low molecular weight aldehyde or ketone. The source of the latter, whether diluent or growing polymer, is still uncertain. Though the data obtained at 185°F were few, they indi-

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(24) Yu. I. Pecherskaya and V. B. Kazanskii, *Dokl. Phys. Chem.*, **162**, 476 (1965).

(25) B. Wunderlich, *Fortschr. Hochpolym. Forsch.*, **5**, 568 (1968).

(26) P. Ingram and A. Schindler, *Makromol. Chem.*, **111**, 267 (1968).

(27) A. Clark, *Ind. Eng. Chem.*, **59**(7), 29 (1967).

(28) W. Dahlig, S. Benbenek, and B. Deczkowski, *Polimery*, **6**, 283 (1961).

(29) L. M. Baker and W. L. Carrick, *J. Org. Chem.*, **33**, 616 (1968).

cate that at the higher temperature the chemisorbed species is capable of forming a stronger bond with the polymerization centers and thereby permanently deactiving them.

In comparing the GPC curves for polymer produced in both phases of the study, it appeared that the presence of oxygen resulted in a product of substantially higher molecular weight. This suggests that oxygen cannot function as a chain transfer agent and that the ratio of propagation to termination at active sites may increase as the number of sites is decreased. These molecular weight data, however, were not unambiguous since the effects of local overheating, which was clearly evidenced in some runs, made it difficult to determine what was truly representative of the intended reaction conditions.

The problem of local overheating arose primarily because the low sensitivity of the mass flowmeter necessitated relatively high rates of ethylene consumption, 500–1000 ml/min. By comparing these values (on a mass/volume/time basis) with consumption rates observed in previous studies[9] conducted at similar temperatures and pressures, it was determined that the present rates were not limited by the rate at which ethylene could dissolve in the diluent. As pointed out above, however, other mass transfer processes may have become significant during the later phases of those runs in which there was a large accumulation of polymer. Hence, concern is especially warranted in those instances when the product contained agglomerated or fused material.[30] Several recent papers[31-33] citing the importance of diffusion and heat transfer in Ziegler-type polymerizations tend to confirm the above concerns and to point up the need for more study of these phenomena in the supported chromium oxide polymerization system.

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(30) A reviewer has pointed out that in the slurry type polymerizations reported here the use of poorer solvents for polyethylene, such as *n*-hexane, is to be preferred.

(31) W. R. Schmeal and J. R. Street, *AIChE J.*, **17**, 1188 (1971).

(32) W. R. Schmeal and J. R. Street, *J. Polym. Sci., Polym. Phys. Ed.*, **10**, 2173 (1972).

(33) C. McGreavy, *J. Appl. Chem. Biotechnol.*, **22**, 747 (1972).

Quenching of Singlet Molecular Oxygen by Polyolefin Additives in Carbon Disulfide Solution

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ABSTRACT: Certain nickel chelates used in stabilizing polyolefins are highly efficient quenchers of singlet oxygen in carbon disulfide solution. The rate constants for quenching by bis[2,2′-thiobis(4-*tert*-octylphenolato)]nickel(II), [2,2′-thiobis(4-*tert*-octylphenolato)](*n*-butylamine)nickel(II), and (di-*n*-butyldithiocarbamate)nickel(II) are 5×10^8, 1.5×10^8, and 40×10^8 M^{-1} sec^{-1}, respectively; the rate constant for (di-*n*-butyldithiocarbamate)zinc(II) is 0.2×10^8 M^{-1} sec^{-1}. The $^1\Delta$ oxygen is produced by flash photolysis with conventional apparatus of oxygen-saturated carbon disulfide solutions containing Methylene Blue as sensitizer, and quenching rate constants determined by monitoring the disappearance of the acceptor, 1,3-diphenylisobenzofuran, at 435 nm.

A mechanism for the photodegradation of polyethylene has been proposed by Trozzolo and Winslow.[2a] One step in this mechanism involves the reaction of singlet oxygen ($^1\Delta$) with vinyl groups to form hydroperoxides. This proposal is supported by the detection of hydroperoxides at the surface of *cis*-polybutadiene after treatment with oxygen ($^1\Delta$).[2b] Hydroperoxide is also formed when singlet oxygen reacts with 1-docosene and *n*-tetracosane; in addition, there is evidence for attack at saturated carbon atoms in the polyethylene chain.[3]

If reaction of oxygen ($^1\Delta$) with polyolefins makes a significant contribution to their overall photodegradation, it should be possible to provide some protection by addition to the polymer of compounds which can efficiently quench singlet oxygen. This approach does not appear to have been intentionally adopted, but it is possible that some commercial polyolefin additives owe part of their effectiveness to their ability to quench singlet oxygen. To test whether this is a reasonable possibility, we have determined the effect of certain additives on the quenching of singlet oxygen in solution. The additives examined were the highly effective polyolefin stabilizers,[4] bis[2,2′-thiobis(4-*tert*-octylphenolato)]nickel(II), [2,2′-thiobis(4-*tert*-octylphenolato)](*n*-butylamine)nickel(II), and (di-*n*-butyldithiocarbamate)nickel(II); the zinc chelate, (di-*n*-butyldithiocarbamate)zinc(II) and the free ligand, 2,2′-thiobis(4-*tert*-octylphenol) were also examined.

Experimentally, it was convenient to study the influence of the chelates on the decay of singlet oxygen in carbon disulfide solution. A number of groups[5-9] have shown that the lifetimes of oxygen ($^1\Delta$) in various solvents can be measured by analysis of the disappearance of the acceptor, 1,3-diphenylisobenzofuran (DPBF). They used pulsed ruby lasers to excite a sensitizer such as Methylene Blue in air or oxygen-saturated solutions, and the singlet

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(1) Chemistry Department, University of Glasgow, Glasgow, W.2, Scotland.

(2) (a) A. M. Trozzolo and F. H. Winslow, *Macromolecules*, **1**, 98 (1968); (b) M. L. Kaplan and P. G. Kelleher, *Science*, **169**, 1206 (1970).

(3) M. L. Kaplan and P. G. Kelleher, *J. Polym. Sci., Part B*, **9**, 565 (1971).

(4) O. Cicchetti, *Advan. Polym. Sci.*, **7**, 70 (1970).

(5) (a) P. B. Merkel and D. R. Kearns, *Chem. Phys. Lett.*, **12**, 120 (1971); (b) P. B. Merkel and D. R. Kearns, *J. Amer. Chem. Soc.*, **94**, 7244 (1972).

(6) C. S. Foote, E. R. Peterson, and K.-W. Lee, *J. Amer. Chem. Soc.*, **94**, 1032 (1972).

(7) I. B. C. Matheson and J. Lee, *Chem. Phys. Lett.*, **14**, 350 (1972).

(8) D. R. Adams and F. Wilkinson, *J. Chem. Soc. Faraday Trans. 2*, **68**, 586 (1972).

(9) R. H. Young, D. Brewer, and R. A. Keller, *J. Amer. Chem. Soc.*, **95**, 375 (1973).