

# Characterization of Oxidized LDPE by Solid State Fluorescence Spectra

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## Synopsis

The fluorescence excitation and emission spectra of commercial LDPE and oxidized LDPEs using phase transferred permanganate as oxidant have been examined using solid state fluorescence spectra. The luminescent impurity species present in commercial polyethylene is found to be olefinic dione. LDPE has an emission spectra at 330–345 nm and excitation spectra at 235 and 300–310 nm. The emission spectra of oxidized LDPEs contain two main peaks, one at 290–300 nm and the other at 330–345 nm. A comparison of the emission spectra of LDPE blends with the reference compounds, viz., stearic acid and stearone, with those of the oxidized LDPEs proves the presence of “saturated” keto groups (carbonyl in the main chain not conjugated with C = C) in oxidized LDPEs. This also enables us to find out quantitatively the amount of the keto groups present. The estimates thus obtained tally with the results of FT-IR measurements and follow the increasing order of the stability constant of the permanganate ionpair in benzene.

## INTRODUCTION

Oxidized polyethylenes, both low density and high density, are known to contain peroxides, various oxygen-containing groups, and unsaturation due to double bonds.<sup>1,2</sup> To characterize the extent of oxidative degradation, quantitative determination of the functional groups is necessary. During oxidation of polyethylene and polypropylene different carbonyl containing groups always appear and their quantities increase monotonically as the oxidation proceeds.<sup>3–5</sup> Therefore, a close correlation exists between the extent of degradation and the intensity of absorption occurring due to C = O stretching vibration in the IR spectrum of the polymer. The different kinds of carbonyl compounds, viz., keto, carboxyl, enone, ester, etc. cannot be detected, however, directly from the IR spectra because the absorption bands of the different oxygen-containing groups are not sufficiently separated. Several workers attempted the simultaneous determination of the different oxo groups by using IR spectroscopy. Cheng and co-workers<sup>6</sup> investigated oxidized polyethylene employing <sup>13</sup>C-NMR. Cooper and Prober<sup>7</sup> neutralized the acid groups of oxidized polyethylene and then estimated the ketones by IR spectroscopy. Inserting a wedge of carbon monoxide ethylene copolymer in the reference beam and thus by compensating the absorption of keto groups, Benham and Pullukat<sup>8</sup> determined spectroscopically the keto groups in the presence of carboxylic groups. Recently Fodor et al.<sup>9</sup> used a combined chemical and infrared spectrophotometric method for the simultaneous determination of concentrations of carboxyl, ketone, and ester

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groups formed in the oxidation of polyethylene. We have determined quantitatively the carboxyl groups present in oxidized LDPEs by using nonaqueous acid-base titration method.<sup>10</sup> To determine the keto and enone (or olefinic dione) groups in the presence of other oxo groups, the technique of fluorescence spectroscopy in solid state has been applied. In this paper we have described a method developed for quantification of "saturated" keto groups present in oxidized LDPEs.

The luminescence spectroscopy has been utilized for a while for identification of polymers. Allen et al.<sup>11</sup> reported that the luminescent impurity species present in commercial polypropylene are enone and dienone. They ascribed the fluorescence emission (excited by radiation of 270 nm) primarily to the presence of the enone and the phosphorescence to the dienone chromophoric units. But the report did not include any quantitative estimation. Charlesby and Partridge<sup>12</sup> had earlier identified the luminescence centers in commercial polyethylene samples (with and without additives) as carbonyl groups attached to the molecular chains (excited with a mercury lamp at 253.7 nm). For the purpose of estimation we have constructed calibration curves from the emission spectra of LDPE blends of stearic acid and stearone chosen as reference compounds. By comparing the emission spectra of the oxidized LDPEs to the reference curves the luminescing moieties have been identified and an estimation of "saturated" keto groups has been made.

## EXPERIMENTAL

### Materials

Commercial low density polyethylene (Alkathene WNC 71) sample in form of beads was supplied by ICI (P) Ltd., India. They contained standard amount of commercial antioxidant (unspecified). All the chemicals employed except stearic acid and stearone were of standard laboratory reagent grade and were used without further purification. Stearic acid (BDH) was recrystallized from ethanol. Stearone was prepared from magnesium stearate by the method given in the literature.<sup>13</sup>

### Oxidation of LDPE

The details of oxidation of LDPE carried out with phase transferred permanganate (purple hydrocarbon) have been reported elsewhere.<sup>10,14</sup> The reagent was prepared in high yield by adding solid phase transfer catalyst to a large excess of aqueous  $\text{KMnO}_4$ , containing 10% NaCl and extracting out with a definite volume of benzene. For oxidation LDPE was refluxed in benzene with the reagent for 6 h. Different phase transfer catalysts used for oxidation are tetrabutyl ammonium bromide (TBAB), tetrapentyl ammonium iodide (TPAI), dicyclohexyl-18-crown-6 (DC-18-C-6), and benzyl triphenyl phosphonium chloride (BTPC). TBAB and TPAI are Kodak Chemicals and DC-18-C-6 is from Aldrich Chemicals Ltd. BTPC has been prepared from triphenyl phosphine (M & T Chemicals Inc.) and benzyl chloride (Aldrich) using standard procedure.

### Spectral Measurements

The IR, FT-IR, absorption, and fluorescence spectra of oxidized LDPEs both in powder and film form were taken.

Fluorescence excitation and emission spectra in transmission mode were recorded using a Perkin-Elmer MPF-44 B fluorescence spectrophotometer. The excitation spectra for all the samples were recorded in the range 200–320 nm with the emitting radiation at 340 nm. The other operating parameters were as follows: slit at  $E_x/E_m = 2/12$ , chart speed = 60 nm/min.

All the emission spectra were recorded in the range 270–400 nm at an excitation wavelength of 230 nm and with the slit at  $E_x/E_m = 12/5$ . The signal gain was kept constant through an entire set of experiments. At least three to four spectra were drawn for each sample and the mean spectrum was deduced.

For quantitative estimation in fluorescence study, the polymer films were used. Since the scattering from the powdered samples could not be totally eliminated, the spectra of the powdered polymer blends were often irreproducible and hence the films were preferred. The sample film was analyzed at an angle of 45° to the beam of excitation light in order to prevent any scattered light from entering the emission monochromator.

### Preparation of Polymer Film

To prepare films, 10% blend of oxidized LDPE was melted in a desk brabender at 130°C and the films were drawn at a constant pressure through an attached accessory. The brabender ensures uniform film thickness. Different cuts of the films (both oxidized and unoxidized LDPE) and different orientations give essentially the same spectral profiles, thereby indicating a large degree of homogeneity.

Films of LDPE and oxidized LDPE prepared manually from toluene solution by slow evaporation of the solvent show spectral profiles identical to those given by the films prepared from the brabender.

### Construction of the Calibration Curve

To draw the calibration curves of stearone and stearic acid, LDPE blends were prepared varying the amount of substrates. All the films prepared with stearone and oxidized LDPEs were transparent but the stearic acid blends became milky in appearance. For each composition at least two blends were made and from each blend several films were drawn. The intensity values quoted were the averages of measurements taken with four to six such films which gave the same spectral profiles and peak areas within 1% of one another.

Since stearone is a long chain aliphatic ketone, it blends well with LDPE and such a blend simulates a structure of "saturated" keto groups in a LDPE backbone. Likewise, stearic acid-LDPE blends conform to carboxyl containing LDPE.

## RESULTS AND DISCUSSION

According to Charlesby and Partridge,<sup>12</sup> the luminescence of polyethylene cannot be a property of the pure polymethylene chain as saturated hydrocarbons

are nonluminescent; the presence of some type of unsaturation is essential. They suggested that the double-bonded chemical impurities like unsaturation in polymer chains or oxidation products and probably keto groups are responsible. Indeed the carbonyl group on account of its  $\pi$  electron bond and non-bonding electrons on the oxygen atom can interact with a variety of adjacent  $\pi$  and/or  $n$  orbitals. Thus a variety of luminescence behavior patterns can be obtained depending on the nature of the moiety concerned. This fact was confirmed later by Allen et al.,<sup>11</sup> who inferred from the absorption spectra of a few model compounds that commercial polyolefins contain chromophores such as keto and  $\alpha, \beta$  unsaturated keto as luminescent impurities.

Fluorescence excitation of LDPE (Fig. 1) shows two distinct peaks, a sharp band at 235 nm and a relatively broad band near the 300–310 nm region. The Woodward-Fieser rules for absorption of enone predict the occurrence of two peaks, one around 235 nm and the other near 320 nm. The absorption corresponding to electron promotion from the carbon-carbon  $\pi$  system to the antibonding  $\pi^*$  orbital of the carbonyl group is found in the region of 220–250 nm. The band in the region 310–330 nm is assigned to the displaced  $n \rightarrow \pi^*$  transition of the carbonyl group and is usually found to be weaker than the

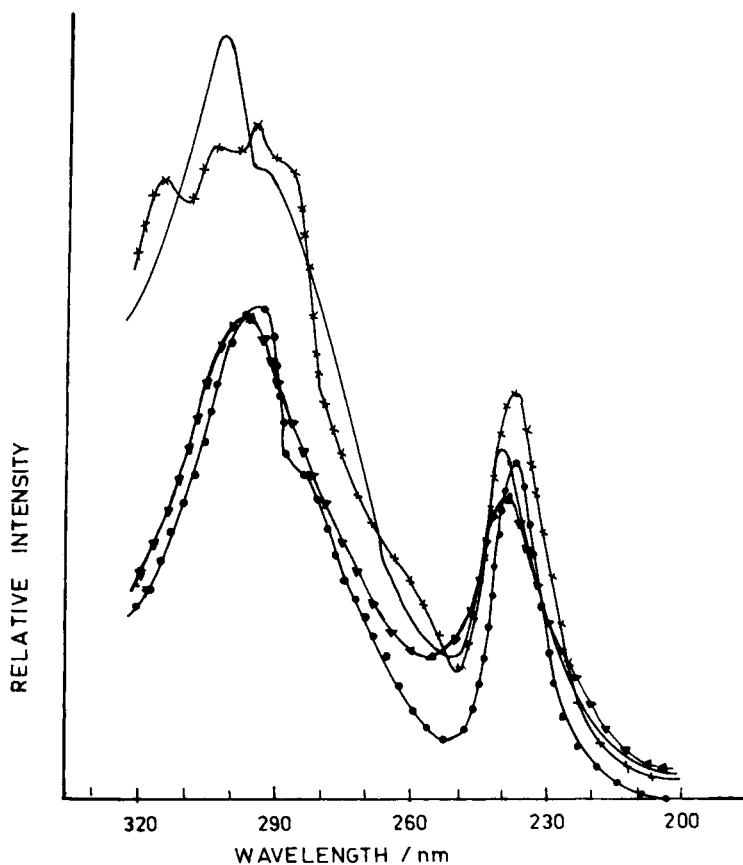


Fig. 1. Fluorescence excitation spectra of LDPE film (-●-●-); oxidized LDPE film (-x-x-); stearone-LDPE blend (—); stearic acid-LDPE blend (-▲-▲-).

$\pi \rightarrow \pi^*$  transition. A perusal of any treatise<sup>15</sup> on UV spectroscopy of organic compounds reveals that methyl vinyl ketone in alcohol solution shows absorption peaks at 213 and 320 nm, 3-methyl-3-pentene-2-one in ethanol absorbs at 236 nm and for 1-acetylcyclohexene two peaks are observed at 233 and 308 nm. Hence  $\alpha, \beta$  unsaturated ketone can be considered as one chromophore present in LDPE. All the oxidized LDPEs, stearone-LDPE blends and stearic acid-LDPE blends have similar excitation spectra. However, our systems show one startling difference from the above-mentioned enones or even from the fluorescence excitation spectrum of polypropylene.<sup>11</sup> The 300 nm band equals or even exceeds the short wavelength band in intensity (see Fig. 1). The oxidized LDPE gives two additional peaks of considerable intensity at 310 and 320 nm. Whenever the chromophore is a dione with one or more vinylene groups the  $n \rightarrow \pi^*$  transition becomes more intense than the  $\pi \rightarrow \pi^*$  transition. For example, 5-heptene-2,4-dione-5 methyl (trans) in EtOH absorbs at 234 nm ( $\log \epsilon = 3.76$ ) and 303 nm ( $\log \epsilon = 4.09$ ); in case of 6-octene-3,5-dione (trans) in EtOH the  $\lambda_{\max}$  and the corresponding  $\log \epsilon$  values are 238 nm, 3.70 and 306 nm, 4.18 respectively.<sup>16</sup> All the LDPE samples (both oxidized and unoxidized) show the vinylidene peak at  $890 \text{ cm}^{-1}$  and trans-vinylene peak at  $990 \text{ cm}^{-1}$ . The oxidized polymers also possess vinyl groups<sup>17</sup> (see Table III). Obviously the oligomers containing multiple carbonyl and olefinic groups (which may or may not be conjugated) will remain on the surface of the polymer and will respond to the exciting radiation. Hence the spectral motifs arise from the combination of several spectra around the same frequency regions. It is even conceivable that the  $\pi \rightarrow \pi^*$  transition in some such conjugated systems may be red-shifted to overlap with the  $n \rightarrow \pi^*$  band.

Fluorescence emission of LDPE shows a broad band in the region 330–345 nm. Oxidized LDPEs also exhibit emission bands in the same region, in addition to a sharp band in the 290–300 nm region. Stearic acid blends with LDPE produce no additional peaks other than those of LDPE. However, a comparison of the emission spectra of stearone-LDPE blends (Fig. 2) and oxidized LDPEs reveals that the two spectra are quite similar.

The fluorescence characteristics of various polymers and polymer blends are compiled in Table I. The emission spectra of the oxidized LDPEs comprise several weaker peaks and shoulders besides the two main peaks. LDPE oxidized with TBAB catalyst gives a larger number of signals, some of which do not appear in the other three oxidized polyethylenes. From IR studies of the products we have hypothesized<sup>17</sup> that the mechanistic pathway followed in TBAB catalyzed oxidation is essentially different. While intermolecular hydrogen abstraction is the primary mode of chain propagation in this case, intramolecular hydrogen abstraction reactions occur with the other three phase transfer catalysts. As a result, different functional groups are generated, and their relative arrangements also differ. In other words, the carbonyl groups obtain in varying molecular environments. Both polystyrene and polyethylene<sup>12</sup> show fluorescence spectra in the same wavelength region; the interval between the vibrational structures in both cases agree with the carbonyl stretching frequencies of alkyl aryl ketones. The acetone fluorescence spectrum is known to be partly due to biacetyl<sup>18</sup>; so a dialkyl ketone cannot be the chromophore in polyethylenes. However, if one or more carbonyl groups are conjugated with olefinic group(s) or peroxy groups are present in one of the neighboring molecular chains, the

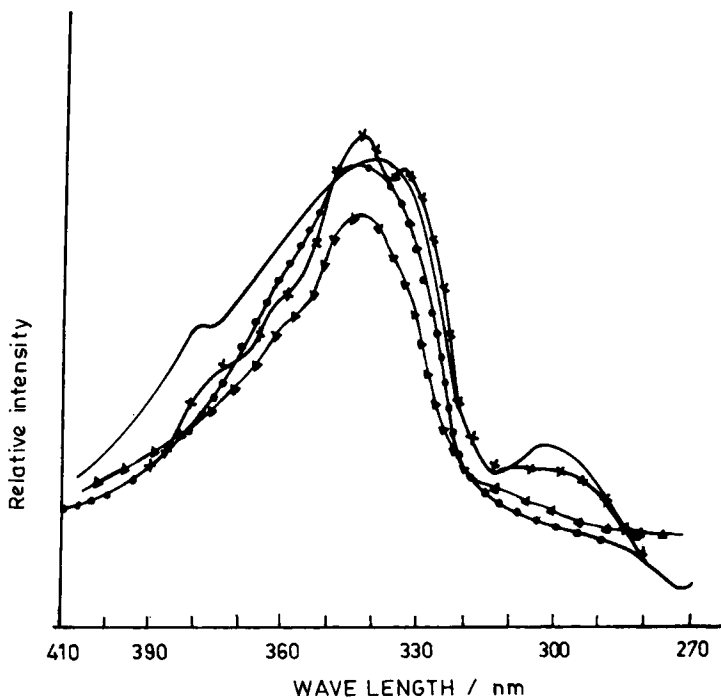


Fig. 2. Fluorescence emission spectra of LDPE film (-●-●-); oxidized LDPE film (-×-×-); stearone-LDPE blend (—); stearic acid-LDPE blend (-▲-▲-).

fluorescence modes will differ from each other. The triplet states which give rise to the fluorescence will be populated by a singlet-singlet absorption of varying energy followed by slightly differing intersystem crossings.

Despite differences in wavelengths of the exciting radiation and the instrument used the fluorescence peaks observed in the present study are surprisingly similar to those reported in the literature (see Table I). This endorses the idea that it is primarily the  $\pi^* \rightarrow n$  transition of the carbonyl group which causes the fluorescence emission in polyethylenes. The differences can be attributed to the impurities initially present in the LDPE samples. The peak positions tally with those for the olefinic diones and the dienones.

Charlesby and Partridge<sup>12</sup> studied the luminescence behavior of LDPEs in commercial forms free of additives and in the presence of varying amounts of different antioxidants. With alkathenes free of additives temperature ( $> 90^\circ\text{C}$ ) aging brought about changes in the intensity of the peaks, while in the presence of antioxidants the spectral profiles remained invariant. They reported "the short fluorescence wavelength, the shortest thermoluminescence wavelength (UV component) and the excitation wavelength limits for spectra A and D, all at around 3000 Å." In the work of Allen et al.,<sup>11</sup> the low density polyethylene samples (not specified) taken were all devoid of commercial additives. But they did not mention the aging behavior of the luminescence signals. In the present study LDPE (Alkathene WNC 71) was found to give stable luminescence peaks over a period of 1 month at room temperature. The oxidized polyethylenes were equally stable, with respect to UV irradiation up to 6 h at room temperature.

TABLE I  
Fluorescence Characteristics of Various Polymers

Polymer	Condition	Excitation wavelength (nm)	Emission wavelength (nm)	Reference no.
LDPE (Alkathene WNC 71)	Powder	230	285, 380-390	Present work
LDPE (Alkathene WNC 71)	Film	230	330, 340, 360	Present work
LDPE (Alkathene WNC 18)	Film	253.7	331, 350, 367, 387	12
LDPE	Powder	265, 300	335(s), 350	21
LDPE	Film	273	295(s), 310, 329(s), 354(s), 370(s)	21
Oxidized LDPE	Powder	230	285, 385, 392	Present work
Oxidized LDPE using TBAB catalyst	Film	230	295, 305, 325, 335, 350, 358, 375, 385	Present work
Oxidized LDPE using TPAI catalyst	Film	230	295, 330, 340, 360, 372	Present work
Oxidized LDPE using DC-18-C-6 catalyst	Film	230	290, 330, 340, 360, 372	Present work
Oxidized LDPE using BTPC catalyst	Film	230	295, 330, 340, 370	Present work
LDPE-stearone blend	Film	230	290, 330, 340, 360, 372	Present work
LDPE-stearic acid blend	Film	230	330, 340, 362	Present work

(s) denotes shoulder.

The fine structures are not obtained in the spectra of the powdered polyethylenes. It is well known in solid state fluorescence spectroscopy that the additional dissipation of energy can occur in powder through scattering from solid surfaces and absorption of exciting radiation dependent on particle size. To avoid excessive scattering, the powdered sample was diluted with calcium carbonate in our experiments. This is equivalent to adding a nonpolar solvent to an emitting solution. The net result would be a blue shift of the emission bands and an overlapping of peaks to give broad band envelopes, as mentioned here.

Allen et al.<sup>11</sup> surmised that the fluorescence emission band of polypropylene at 340 nm is due to the  $\alpha$ ,  $\beta$  unsaturated carbonyl groups. On the other hand, Charlesby and Partridge<sup>12</sup> have compared the phosphorescence spectra of Alkathene WNC 18, Alkathene 2, and Alkathene 7 to those of acetone, di-*a*-butyl ketone, and a series of aldehydes. They have concluded that carbonyl groups and main chain unsaturation are the luminescence centers. The band found at 330-345 nm in LDPE and oxidized LDPEs can be assigned to the presence of

enone species. With reference to the spectra of stearone blends the new emission band appearing in the region 290–300 nm is attributed to the “saturated” keto groups. Moreover, stearic acid LDPE blends do not show any characteristic peak in this region. The term “saturated” keto group is ascribed to a carbonyl in the main chain not conjugated with a C=C double bond; this does not rule out the possibility of having vinylene in one of the chains associated with the carbonyl group.

The analytical use of fluorescent spectroscopy lies in the linearity of the intensity–concentration relationship which is expressed as

$$(S_f)_\lambda = f(\theta)g(\lambda)I_0\phi_fAbC \quad (1)$$

for low concentration of fluorescent material, where  $(S_f)_\lambda$  is the sample fluorescence intensity at a given wavelength  $\lambda$ ,  $f(\theta)$  is the geometry depending on the effective solid angle used by the detector,  $g(\lambda)$  is the response characteristic of the detector (varies with  $\lambda$ ),  $I_0$  is the intensity of the exciting radiation,  $\phi_f$  is the quantum efficiency of the molecule,  $A$  is the molar absorptivity for the sample at the exciting wavelength,  $b$  is the sample path length along the axis of irradiation, and  $C$  is the concentration of the fluorescing material (mol/L).

Thus for a given instrument and under fixed experimental conditions

$$(S_f)_\lambda = KC \quad (2)$$

where  $K = f(\theta)g(\lambda)I_0\phi_fA \cdot b$ . The quantities  $f(\theta)$ ,  $g(\lambda)$ ,  $I_0$ , and  $b$  are instrument parameters and are manipulated to remain constant. On the other hand,  $A$  and  $\phi_f$  will depend on the nature of the absorbing molecule and the absorption process. Presumably the “saturated” keto moiety which is supposed to be the absorbing species at the wavelength considered (295–300 nm) behaves identically in all samples irrespective of the length of the segment or other structural environments.

Pollack's<sup>19,20</sup> theory for luminescence of solid surfaces with strong scattering and relatively large absorbance gives a relation between the intensity of fluorescence in transmission mode and fluorescer properties:

$$(S_f)_\lambda = \frac{FC I_0}{2} \exp(-\gamma_F)(1 - Q_B^2)(1 + Q_F) \quad (3)$$

where  $(S_f)_\lambda$  is the intensity of transmitted fluorescence at a given wavelength  $\lambda$ ,  $I_0$  is the intensity of exciting radiation,  $F$  is the coefficient of fluorescence of the material/component,  $Q$  is the coefficient of reflectance of a sheet of medium thick enough so that its transmission is negligible,  $C$  is the amount of fluorescer, and  $\gamma$  is the natural log of transmittance of a very thin sheet with no reflectance.

It has been shown<sup>19</sup> that  $Q$  and  $\gamma$  terms are usually very small in transmitted fluorescence. Hence, the intensity is a linear function of concentration, and almost independent of distribution of concentration in the film. The signal-to-noise ratio is also constant<sup>20</sup> and independent of  $C$ .

Utilizing the linear relation between  $(S_f)_\lambda$  and  $C$ , it is possible to construct the calibration curve of fluorescence intensity vs. concentration of the fluoresc-



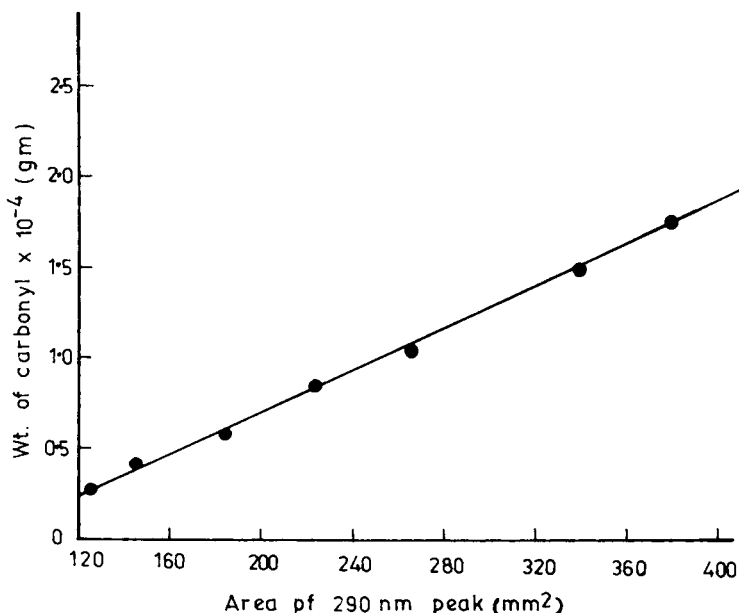
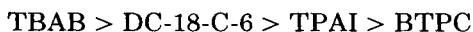


Fig. 3. Calibration curve of stearone-LDPE blend.

ing species. From the data on stearone-LDPE blends, the area of the 290–300 nm peak,  $(S_f)_\lambda$ , was plotted against the total keto concentration (wt %), and a linear graph (Fig. 3) was obtained. Comparing the emission spectra of oxidized LDPEs with calibration curve, the keto content of those samples were calculated. From the results (see Table II) it is evident that the oxidized LDPE using TBAB catalyst has the maximum number of keto groups vis-à-vis the other oxidized LDPEs. The decreasing order of the keto groups found in different oxidized LDPEs is correlated to the phase transfer catalyst as follows:



Similar results have been obtained from the FT-IR spectra.<sup>17</sup> On oxidation, various absorption peaks appear in the carbonyl stretching region between 1685 and 1785  $\text{cm}^{-1}$ . All the oxidized polyethylenes are, of course, characterized by the predominant 1715  $\text{cm}^{-1}$  absorption of an isolated carbonyl group on a

TABLE II  
Determination of Percentage Carbonyl Present in Oxidized LDPE

Catalyst used for oxidation	Wt of oxidized LDPE (g) × 10 <sup>-3</sup>	Area of 290–300 nm peak (mm <sup>2</sup> )	Percent of carbonyl
TBAB	3.72	284	3.09
TPAI	5.62	274	1.95
DC-18-C-6	3.92	233	2.22
BTPC	3.43	139	1.45

polyethylene chain.<sup>4</sup> By taking the peak at  $1460\text{ cm}^{-1}$  of the  $\text{CH}_2$  group as the internal standard, the relative peak intensities have been calculated<sup>17</sup> for different functional groups for quantitative determination of these groups. It is observed that the use of different catalysts affect appreciably the intensities of isolated carbonyl groups at  $1710\text{ cm}^{-1}$  in the oxidized product. The relative intensities of carbonyl groups have decreased in the following order:

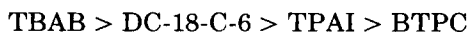


Table III compares the data of carbonyl content found from two different measurements, e.g., fluorescence studies and FT-IR studies. It also includes the stability constant values for different oxidants and the percentage carboxyl content determined by nonaqueous acid-base titration of different oxidized LDPEs. With maximum carboxyl content, LDPE oxidized under BTPC catalyst shows a minimum number of keto groups in it. This is an indirect evidence of the fact that carboxylic acid group does not take part in fluorescence emission. The FT-IR results are expressed as ratios while the fluorescence studies express the keto content directly as the weight percentage. It is gratifying to note the similarity in the two orders despite the important difference in units and dimensions. Interestingly, the "saturated" keto content of the oxidized LDPE increases in the same direction as the stability constant of the permanganate ionpair in benzene.

The broad peak found in case of LDPE in the region 330–345 nm increased in intensity in the case of all the substrates but not proportionately with the percent content of the substrate. This behavior can be explained if one considers the changes in quantum efficiency of the molecule and/or the different molar absorptivities for the sample at this exciting wavelength. Obviously a variety of the enone species are generated in the four oxidized LDPEs depending on the mechanistic pathway<sup>17</sup> followed. Since they are likely to differ in  $\phi_f$  and  $A$  values, there is a deviation from the linearity between the fluorescence intensity and the concentration of the emitting species.

## CONCLUSION

The fluorescence intensity measurements of LDPE films in the 290–300 nm region can be used to estimate the "saturated" keto groups incorporated in the

TABLE III  
Some Properties of Oxidized LDPEs

Catalyst used for oxidation of LDPE	Stability constant <sup>10</sup> of the oxidant	Carbonyl present		Carboxyl <sup>10</sup> present (%)	Olefinic <sup>17</sup> present (%)
		FT-IR results <sup>17</sup> (relative to LDPE)	Fluorescence studies (%)		
TBAB	$23 \times 10^2$	2.69	3.09	8.0	0.094
TPAI	$2.8 \times 10^2$	2.24	1.95	5.5	0.072
DC-18-C-6	$2.3 \times 10^2$	2.34	2.22	15.0	0.176
BTPC	$0.4 \times 10^2$	1.95	1.45	20.0	0.132

polymer by oxidation with phase transferred permanganate. The technique is based on the calibration curve drawn for stearone-LDPE blends and does not suffer from the interference of other oxo groups. The multiple peaks in the UV region are ascribed to the olefinic diones with different molecular chains. The fluorescence patterns result solely from the  $\pi^* \rightarrow n$  transitions of the various carbonyl moieties. LDPE oxidized with TBAB gives a different spectral profile as expected from the distinct mechanism followed.

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