

Oxidation of Low Density Polyethylene (LDPE) By Purple Hydrocarbon

In recent years, a number of heterogeneous methods¹⁻¹² have been developed for oxidizing low-density polyethylene (LDPE) and also the polyolefins in general. However, these entail mixing problems and result in inhomogeneous oxidation. A homogeneous method, on the other hand, can achieve controlled, uniform, and optimal bulk and surface oxidation. The phase transfer catalysts have of late opened the avenues for oxidation at specific sites for a wide variety of organic molecules,¹³⁻¹⁶ but they have never been applied for polymer modification in homogeneous and biphasic systems. We have developed a new method for oxidation of polyolefins which is homogeneous in nature and utilizes a phase transfer catalyst to transfer the oxidant into the hydrocarbon phase. The present communication describes the preliminary investigation regarding the utility of the "purple hydrocarbon" reagent as an effective homogeneous oxidizing agent for LDPE.

EXPERIMENTAL

Materials

Polyethylene samples were supplied by I.E.L. (Chemicals Division). They contained no commercial additives. All other chemicals like potassium permanganate, sodium chloride, and tetrabutyl ammonium bromide were of analytical grade. The solvents, benzene and toluene, were of spectroscopic quality.

PREPARATION OF PURPLE BENZENE

Potassium permanganate (5 g) was dissolved in 30 mL of 10% sodium chloride solution (w/w) and a bright colored solution was obtained. To this, 30 mL of benzene was added. This mixture was vigorously stirred and allowed to stand for a brief period. It was noted that the purple color remained entirely in the aqueous layer. To this, an aqueous solution of tetrabutylammonium bromide (prepared by dissolving 4 g salt in 5 mL of water) was added, and the mixture was vigorously stirred and allowed to stand. The nonaqueous phase which formed the upper layer turned purple. This mixture was called "purple benzene" and used as the oxidizing agent. In a similar manner "purple toluene" was also prepared.

OXIDATION OF LDPE USING PURPLE BENZENE

LDPE beads (10 g) were added to the above mixture and refluxed for 6 h. After the completion of the reaction, the hot viscous solution was added to a large excess of acetone to precipitate out the oxidized LDPE. To remove MnO_2 , the solid mass was digested with concd HCl for 1 h. After removal of MnO_2 it was washed thoroughly and dried under vacuum at 30–40°C to remove the traces of solvent present. It is noteworthy that the presence of traces of water is essential for the reagent to be a potent oxidant.

The acidity of the sample was determined by titrating the polymer solution in benzene ethanol mixture using standardized N/100 ethanolic NaOH solution and phenolphthalein indicator.

IR spectra of the polymer films were recorded in the range 4000–200 cm^{-1} using Perkin-Elmer 298 IR spectrophotometer. Solid state fluorescence spectra of the oxidized LDPE was taken with a Cary 17 spectrophotometer with the incident beam of 230 nm. The powdered sample was smeared inside a Dewar tube which was placed in the cell holder at an appropriate angle to minimize the effect of scattering.

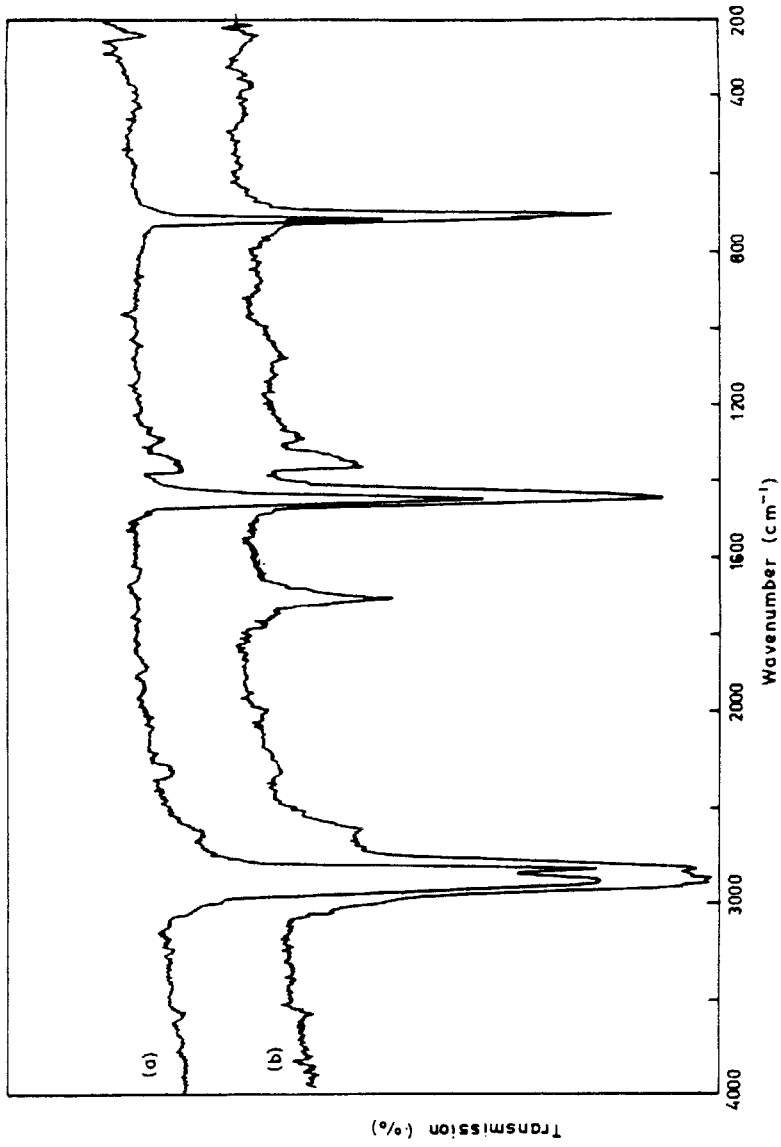


Fig. 1. Infrared spectra of: (a) LDPE; (b) Oxidized LDPE.

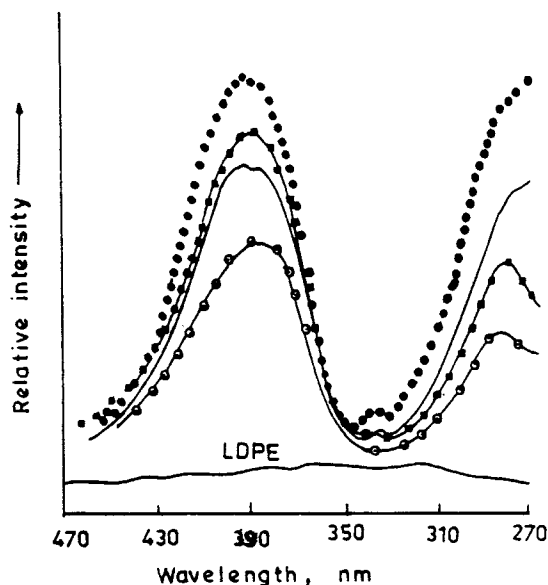


Fig. 2. Solid state fluorescence spectra: (···) 3 h purple toluene; (-■-■-■-) 2 h purple benzene; (—) 6 h purple toluene; (-○-○-○-) 9 h purple toluene.

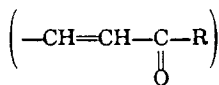
RESULTS AND DISCUSSION

IR Spectra

By comparing the IR data of LDPE and oxidized LDPE two new peaks were observed: one at 1710 cm^{-1} and the other, a broad peak at $1100\text{--}1000\text{ cm}^{-1}$. The 1710 cm^{-1} peak can be assigned to $>\text{C}=\text{O}$ stretching vibration; the $>\text{C}=\text{O}$ function may arise from the carboxyl/ester or the unsaturated carbonyl group. The IR spectra are shown in Figure 1. To examine whether the 1710 cm^{-1} peak is due to ketonic group or carboxyl group, the oxidized LDPE sample was boiled with NaOH solution for 1 h. After thorough washing and drying; the IR spectra of that sample were taken. The position and the profile of the 1710 cm^{-1} peak did not alter appreciably. Thus we can infer the dominating presence of the ketonic group in the oxidized LDPE.

SOLID STATE FLUORESCENCE SPECTRA

The solid state fluorescence data further confirm the presence of both $>\text{C}=\text{O}$ and $-\text{COO}-$ groups. The oxidized LDPE, irrespective of the time of oxidation, shows two peaks at 285 and 392 nm. The relative intensities of two peaks, however, depend on the extent of oxidation (Fig. 2). While the two peaks are comparable for shorter periods of oxidation, the 392 nm band becomes predominant when the time of oxidation is 6 h or more. Allen and McKellar¹⁷ performed fluorescence studies on polyolefins and showed that the emission bands of 295 nm are exhibited by a typical enone compound



Likewise the 392 nm peak can be assigned to $-\text{COO}^-$ as the chromophore because benzoic acid absorbs at 381, 391, 405, and 416 nm.¹⁸

BULK ACIDITY

The bulk acidity as determined by nonaqueous acid-base titration is given in Table I. The results show that the percentage acidity of oxidized LDPE using purple toluene is lower than

TABLE I
Percentage Acidity for Oxidized LDPE Using Different Oxidizing Agents
at Various Times

Oxidizing agent	Time of oxidation (h)	Temperature of oxidation (°C)	Acidity (%)
1. Chromic acid ¹⁹	6	60-70	13.86 ± 0.52
	9		14.03 ± 0.50
	12		14.32 ± 0.48
2. Permanganic acid ¹⁹	4	30	15.41 ± 0.50
3. Purple toluene	6	110	12.88 ± 0.53

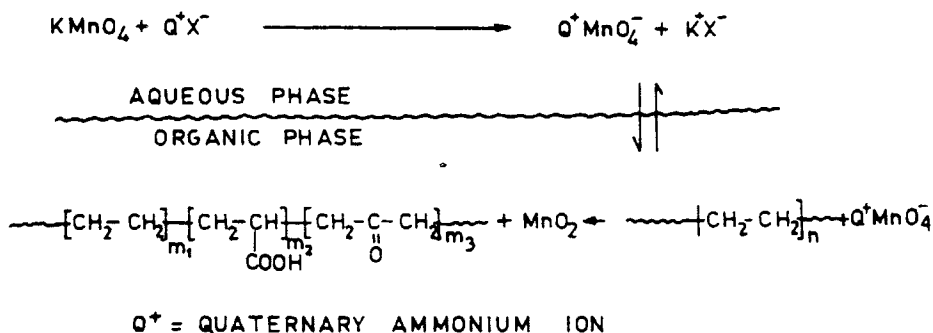


Fig. 3. Possible pathway for the reaction between LDPE and purple hydrocarbon.

these of the products obtained with other two oxidizing agents. This also indicates a large contribution of carbonyl group vis-a-vis carboxyl group. The reaction between LDPE and purple hydrocarbon can be postulated as shown schematically in Figure 3.

As evident from the scheme, tetrabutyl ammonium permanganate is the oxidant. This is also confirmed by the NMR signal of tetrabutyl group and the UV absorption spectra of the permanganate moiety.

In a separate communication we have given a detailed account of the nature of the oxidizing species and its applicability as an oxidant. We have also studied the influence of several other phase transfer catalysts on the formation of "purple hydrocarbon."

In conclusion, our studies show that the purple hydrocarbon can oxidize LDPE in a homogeneous medium, giving rise to both carbonyl and carboxyl groups, although the former is present in a larger proportion.

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