

Oxidation of Polypropylene in a Solution of Monochlorobenzene

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ABSTRACT: The oxidation of polypropylene (PP) was performed in a solution of monochlorobenzene using tetrabutyl ammonium permanganate either in the presence or absence of purified air and dodecanol-1. The experiments were conducted under atmospheric pressure at 128–130°C. The oxidized PP was found to contain polar groups such as carboxylates, carboxylic acids, ketones, esters, etc. as determined by Fourier transform infrared, ultraviolet, nuclear magnetic resonance, and electron spectroscopy for chemical analysis. The presence of the MnO₂ formed upon the decomposition of tetrabutyl ammonium permanganate was determined by electron spectroscopy for chemical analysis. The dodecanol-1 was used as an accelerator for the oxidation reaction of PP in presence of air. Solubility trials of oxidized PP in toluene and methyl ethyl ketone were performed. A reaction mechanism is proposed. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 3417–3424, 1999

Key words: polypropylene; oxidation; monochlorobenzene

INTRODUCTION

Because of the presence of tertiary carbons and unsaturated sites in polypropylene (PP), its oxidation potential is greatly enhanced^{1–3}; furthermore the dissociation energy of a primary carbon C—H bond is about 100 kcal, whereas it is 79 kcal for tertiary carbon C—H bonds.^{4,5}

The oxidation of PP leads to the formation of oxygen-containing groups such as C=O, $\begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{O} \end{array}$, COOH, $\begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{O}^- \end{array}$ and hydroperoxides,⁶ which greatly affect the surface polarity and the adhesion properties of the polymer.^{6–8}

Salts, more particularly salts of transition metals, act as catalysts in the auto oxidation of atactic PP.^{9–16} The oxidation of atactic PP may also be conducted in solvents such as monochlorobenzene or dichlorobenzene¹² at 70–125°C, in the presence of ozone,^{13,14} ditertiary butyl peroxalate,¹⁵ or an aqueous solution¹⁶ of K₂Cr₂O₇/H₂SO₄.

The oxidized PP (OPP) may be used as a compatibilizer in polymer blends; it may also be used as a lubricant or processing aid in certain alloys and composite systems.

In this article we present the results of the oxidation of PP homopolymer in an heterogeneous organic system¹⁷ in the presence of tetrabutyl ammonium permanganate (TBAP), air, and a combination of both.

EXPERIMENTAL

Material

The PP (grade Moplen T30G) used in this work was supplied by Himont Co. of Varennes, Canada.

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Table I Oxidation Conditions of Polypropylene

Trial Number	Polypropylene (g)	TBAP (g)	O ₂ (air)	Dodecanol-1	Temperature (°C)	Reaction Time (h)	Chlorobenzene (mL)	Oxygen Flow (L/min)	Other Conditions
1	2.53	0.5	Yes	No	128–130	6	30	0.5	
2	2.53	0.5	No	No	128–130	6	30	0	Pure N ₂ only
3	4.00		Yes	0.2% by wt	128–130	6 1/2	43	0.5	
4	4.00		Yes	No	128–130	2 1/2	43	0.5	
5	4.00		Yes	No	128–130	4 1/2	43	0.5	
6	4.00		Yes	No	128–130	6 1/2	43	0.5	

The dodecanol-1 was obtained from Merck Chemical Co., Darmstadt, Germany. The potassium permanganate, the tetrabutyl ammonium bromide (TBABr), and the solvents [monochlorobenzene (MCB), methyl ethyl ketone (MEK), methanol, and Toluene] were all of analytical grade and also supplied by Merck Chemical Co. The TBAP was prepared in our laboratory by the following procedure.

Preparation of TBAP¹⁸

Initially, 0.644 g of TBABr is dissolved in 1.8 mL of deionized water. A second solution of 0.316 g of potassium permanganate in 3.5 mL of distilled water is also prepared.

The potassium permanganate solution is added slowly to the tetrabutyl ammonium bromide solution at room temperature under constant agitation. A purple precipitate of TBAP is formed. After 5 min the agitation is stopped and the solution is let undisturbed for 1 h. The solution is filtered and the KBr formed is eliminated by successive washings with 1 mL of cold distilled water. The solid residue is dried under high vacuum for 2 h at room temperature. The conversion yield for the reaction is close to 100%.

Apparatus

The samples were characterized by nuclear magnetic resonance (NMR) (Bruker W. H. spectrom-

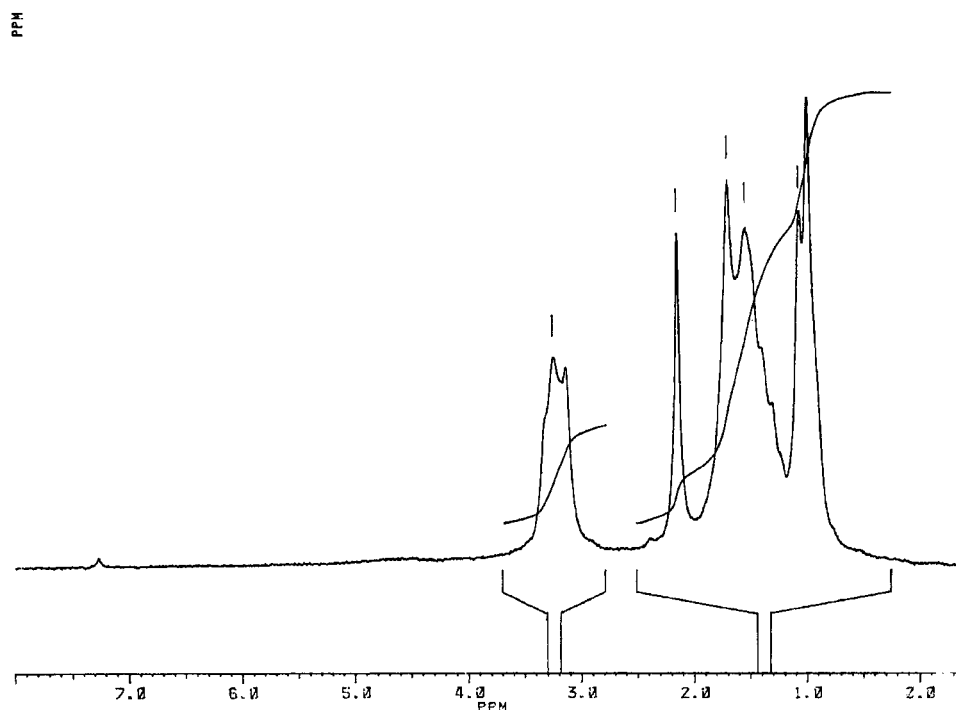


Figure 1 NMR spectrum of TBAP in deuterated chloroform.

Table II Effect of Oxidizing Agent on the Carbon-Oxygen Ratio: ESCA Analysis

Oxidizing Agent	Quantity (mol)	Flow Rate (L/min) of Air	Carbon Atoms (%)	Oxygen Atoms (%)	Manganese Atoms (%)	Ratio of Carbon Atoms to Oxygen Atoms
TBAP and O ₂ (air)	0.0138 (TBAP)	0.5 and 1	98.25	1.75		56.14
TBAP	0.0138 (TBAP)	Under N ₂ atmosphere	94.1	4.6	(1.33) ^a 1.3	20.45
O ₂ (air) and dodecanol-1	0.43 × 10 ⁻³ dodecanol-1	0.5	95.4	4.6		20.73
O ₂ (air)	—	0.5	99.4	0.6		165.66

^a Measured by atomic absorption.

eter, 80 MHz, Bruker Instruments Inc., Billerica, MA), by Fourier transformation infrared (FTIR)-4300 (Shimadzu Scientific Instruments Inc., Columbia, MD), by ultraviolet (Shimadzu UV, visible recording spectro photometer, UV-265 FW) by electron spectroscopy for chemical analysis (ESCA) (Escalab 3 MK II, VG Scientific Ltd., East Grinstead, West Sussex, United Kingdom), by vapor pressure osmometer (VPO) (Knauer, Karl Knauer KG, Biberach, Germany) using toluene as a solvent at 90°C for 5 min with benzil as a calibration solution and using toluene as solvent.

Oxidation of PP

The actual experimental conditions for the oxidation are given in Table I. It was found that the lowest temperature, at which we could solubilize the PP in MCB under atmospheric pressure was 128–130°C.

Purification of Oxidized PP

The oxidation of PP in the presence of TBAP and in the presence or absence of air (O₂) gives a

Table III Polymer Solubilization

Polymer	Oxidation Agent	Solubility in Cold Toluene (W/W %)	Solubility in Warm MEK (W/W %)
PP	None	0	0
OPP	TBAP	18	10
OPP	TBAP + O ₂ (air)	15	6
OPP	O ₂	8	2
OPP	O ₂ + trace of dodecanol-1	12	9

brownish solution containing dark brown particles. The solution is filtered and the filtrate distilled under atmospheric pressure to eliminate the solvent. Once the filtrate is distilled, a solid residue containing OPP and MnO₂ is obtained. Fifty milliliters of boiling toluene is added to the residue and after solubilization the hot solution is poured gradually in five times its volume of boiling methanol. The OPP precipitates out. To avoid the precipitation of MnO₂ from the methanol solution with the OPP, 10 mL of a 2% H₂SO₄ aqueous solution is added. This mixture is held under reflux for 4.5 h until complete discoloration of the particles and the solution. The solution is filtered and the OPP is washed with a 50 : 50 mixture of methanol and water until pH = 7. The OPP is dried under vacuum and under nitrogen atmosphere at room temperature. The polymer obtained is characterized by infrared (IR) and ESCA. The polymer recovered is 94% of the original PP. The presence of MnO₂ before discoloration by an aqueous solution of 2% H₂SO₄ was confirmed by an iodometric test method as well as by the elimination of Cl₂ after a treatment of the MnO₂ sample with HCl which produced a white precipitated Mn (OH)₂ after the addition of an aqueous solution of NaOH. Furthermore, the ESCA analysis indicated signals at 49, 83, 652, and 770 eV because of the 3p, 3s, 2p, and 2s orbitals of the manganese which is in accord with MnO₂.

In the case of oxidation by O₂, in the presence or absence of the accelerator dodecanol-1, after treatment with MCB, the warm MCB solution precipitates when poured in boiling methanol. It is filtered and the white particles are washed with warm methanol (45°C) and dried under vacuum at room temperature. The average

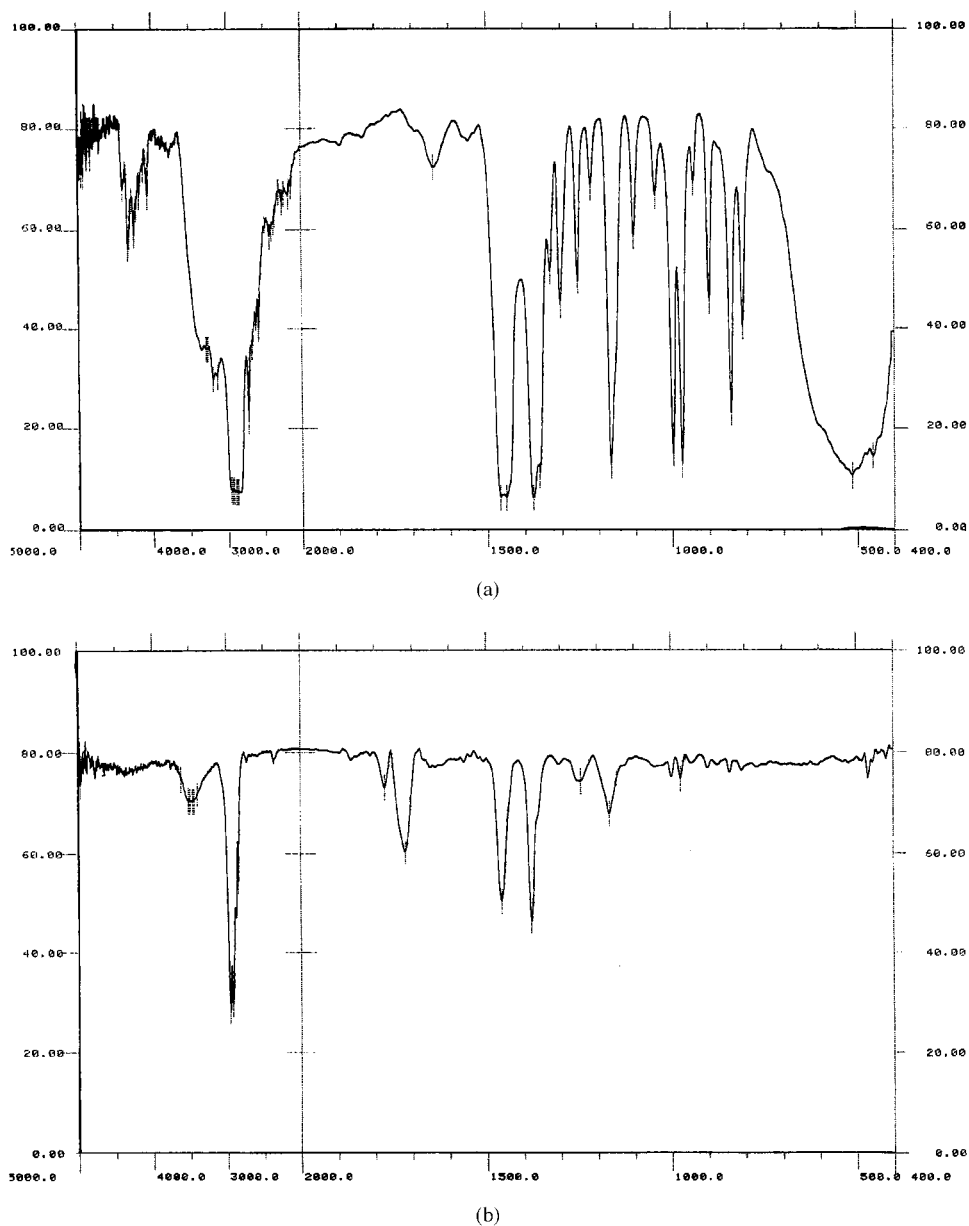
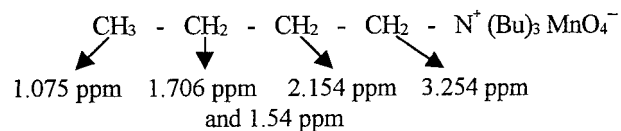


Figure 2 (a) IR spectrum of PP treated by TBAP; (b) IR spectrum of PP treated by TBAP and air (O_2); (c) IR spectrum of PP treated by O_2 in the presence of dodecanol-1.

polymer recovered corresponded to 97% of the original PP.

RESULTS AND DISCUSSION

The TBAP was characterized by NMR and IR. The NMR spectra (Fig. 1) shows the presence of methyl, methylene (from CH_2-N) groups and two other CH_2 groups.



The 1.706 and 1.54 absorptions bands are due to the protons of the CH_2 groups; because they have a diastropic form, they will appear at two different regions. The absorption band at 3.254 ppm is due to $-CH_2N^+$ indicating the presence of

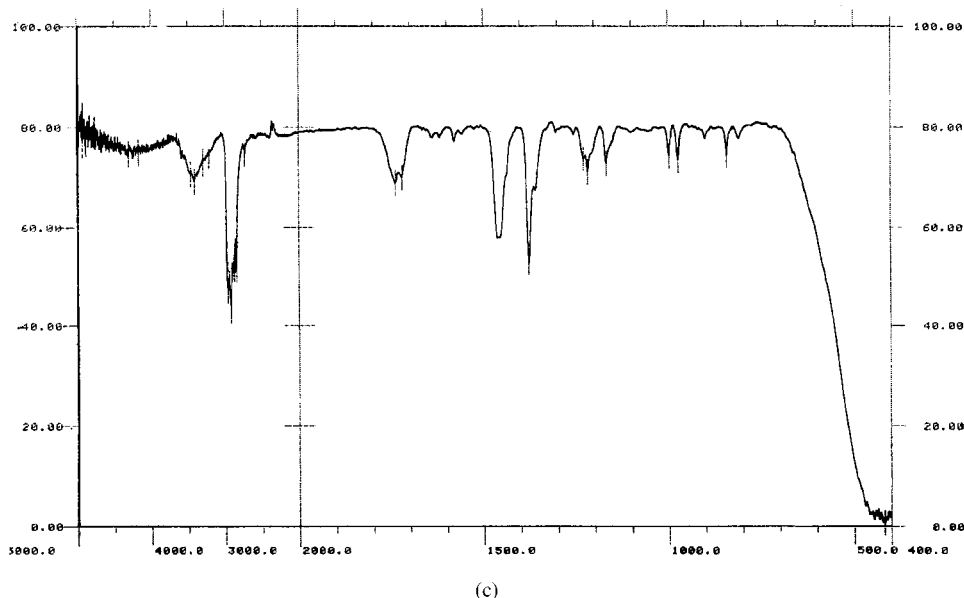


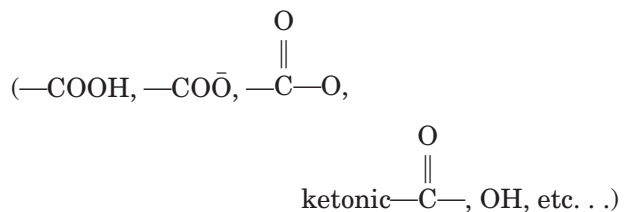
Figure 2 (Continued from previous page)

a quaternary ammonium ion as a permanganate and not as a manganate (MnO_4^-). The existence of the MnO_4^- ion is confirmed by the absorption band at $920\text{--}890\text{ cm}^{-1}$.¹⁹

During the oxidation reaction, the solution of TBAP which is initially purple turning to a yellow-green color after 45 min, then yellow-brown after 2 h, and finally colorless with a brown suspension of MnO_2 . This indicates that the TBAP has reacted completely. The brown particles disappear when either HCl or H_2SO_4 is added to the solution (Mn^{++} salts formation).¹⁹

The quantity of chlorine liberated by the reaction between MnO_2 and HCl was determined by an iodometric method^{20,21} and the number of atoms of Mn was determined by ESCA. This permits obtainment of a qualitative and a quantitative measurement of the MnO_2 formed (Table II).

The oxidation of PP by TBAP, O_2 , or a combination of both will modify the molecular structure of PP. Depending on the oxidizing reaction, one can obtain polar groups



and even promote scission of the polymer chain. This will change the physico-chemical properties of the PP.

Solubility trial showed that the solubility of the OPP varies with the polarity and the type of oxygen groups formed. Before oxidation, PP was insoluble in cold or boiling MEK, whereas after oxidation, we observed a partial solubilization in warm MEK (Table III). Furthermore, the PP is also not soluble in cold toluene; however, after oxidation it is partially soluble (see Table III).

ESCA and FTIR Analysis

The study by ESCA gave interesting results when used to characterize the polyolefins surfaces containing polar groups in the chain²² because it greatly affects the superficial layer C_{1s} of the electronegative elements.^{23,24}

OPP, due to oxygen-containing groups such as C---O , ---C=O , and ---C---O already present in the polymer, will have very sharp ternary peaks. These groups having bond energies of 286.5, 288.0, and 289.5 eV, respectively, will give a signal at 532.0 eV for O_{1s} in all cases.

The percentage of C, O, and Mn on the sample surface, as determined by ESCA, and the ratios between the number of C atoms and the number of O atoms are given in Table II.

The relatively high percentage of oxygen atoms, as determined by ESCA, IR, and FTIR, confirms the existence of ketonic, ester, carboxylic, and alcoholic groups [Figs. 2(a-c)]. The IR spectrum [Fig. 2(a)] of PP treated by TBAP have an

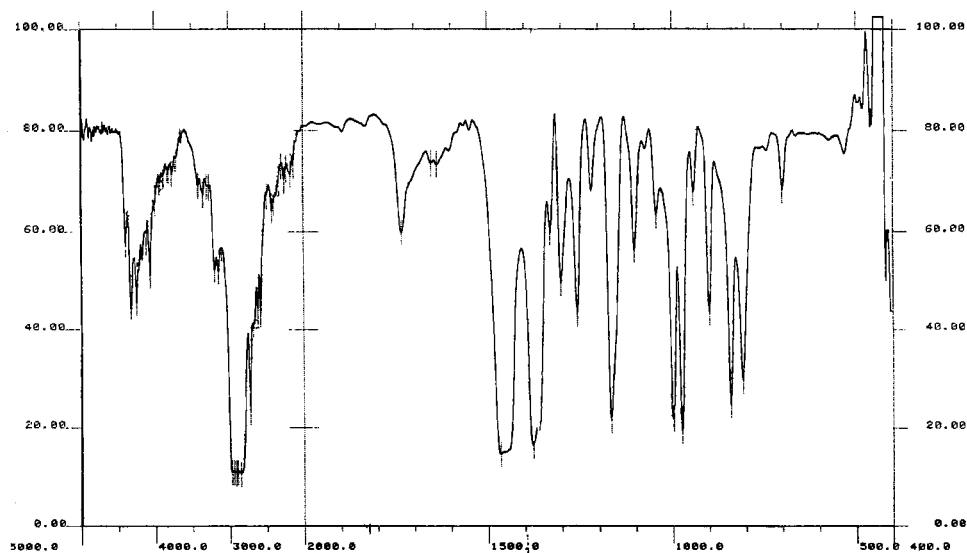


Figure 3 IR spectrum of PP treated by TBAP and HCl.

absorption band at 1641 cm^{-1} and 1167 cm^{-1} attributed to the carboxylate ions. The ESCA and atomic absorption results indicate the presence of Mn atoms (Table II). This suggests that with 1.3% of the atoms being Mn, 4.6% being O, 94.1% being C, and that no nitrogen or ammonium quaternary ion could be found, we have a manganous carboxylate.

The treatment with diluted HCl shows a shift of the absorption band from 1641 cm^{-1} and 1653 cm^{-1} (weak) and 1734 cm^{-1} (strong) which is in agree-

ment with the disappearance of manganous carboxylate and the formation of carboxylic groups (Fig. 3).

The oxidation with TBAP in the presence of O_2 shows the presence of ketones (1710 cm^{-1}), anhydrides, or γ -lactones (1772 cm^{-1}) [Fig. 2(b)] but the oxidation by O_2 and dodecanol-1 shows the presence of ketonic groups at 1720 cm^{-1} [Fig. 2(c)] and esteric groups at 1745 cm^{-1} . There is also a relatively important absorption band at 3469 cm^{-1} which indicates an intramolecular polymeric hydrogen bond [Fig. 2(c)].

Table IV Effect of Oxidation Conditions on PP

Oxidation Conditions	Absorption Bands (cm^{-1})	Chemical Groups Formed	Molecular Weight \bar{M}_n of OPP (VPO)	Surface Tension (dyne/cm)
Reference sample of PP	—	—	187,322 (\bar{M}_n of PP)	29.4
TBAP (before acid treatment)	1166.9, 1641, 1680, 3291	Carboxylate and carboxylic acids	92,830	34.5
TBAP (after acid treatment)	1733	Carboxylic acids	Not determined	Not determined
TBAP and air (O_2) ^a	1772, 1710, 1166.8	Ketones (1710) and anhydrides or γ -lactones	120,391	32.9
Air (O_2) and dodecanol-1	1720, 1745, 1166, and 3469	Ketones, esters, and OH bondings	110,890	33.1
Air (O_2)	1700–1600, 1640, and 3450	Carboxylic acids, ethylenic double bonds, and OH bonding	144,540	30.9

^a There is no change in IR spectra, \bar{M}_n , and surface tension after acid treatment.

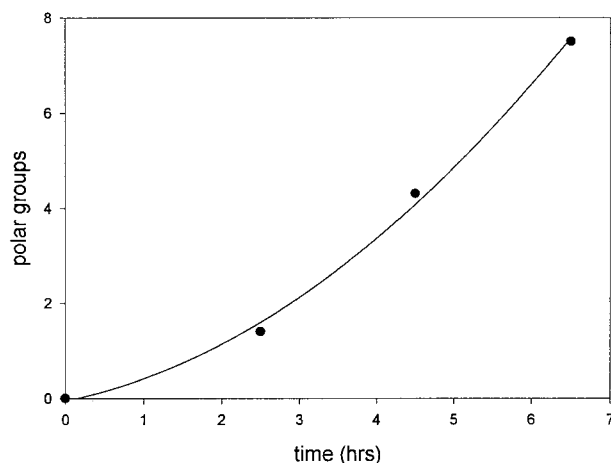


Figure 4 Ratio of areas of absorption bands of PP treated with air as function of time. $1700\text{--}1600\text{ cm}^{-1}/1377\text{ cm}^{-1}$, and $3600\text{--}3100\text{ cm}^{-1}/1377\text{ cm}^{-1}$ vs time.

From Table II, we have a somewhat surprising result: the presence of air has decreased the TBAP oxidative power. This may be due to the dilutive effect by air of atomic oxygen with the polymer matrix and may also be due to an undesirable side reaction. Dodecanol-1 with air will initiate the oxidation reaction and plays the role of an accelerator. In this case, the amount of atomic oxygen (4.6%) in the OPP indicates the oxidation power of dodecanol-1 and air system which is also very interesting. It should be noted that the oxygen atoms do not come from the dodecanol-1 because the quantity of alcohol added is very low (0.2% by weight). It also should be noted that if some oxidized products from dodecanol-1 are produced, they are eliminated during the purification of OPP and the rest is generally soluble in the solvents used (toluene and methanol). After evaporation of the warm nonsolvent solution, a small quantity of oily substance remains. This oily substance becomes a solid at room temperature. The fusion point of this product was $23 \pm 1^\circ\text{C}$ with a boiling point of $255 \pm 1^\circ\text{C}$ which correspond exactly to the dodecanol-1 specifications. The existence of dodecanol-1 at the end of the reaction suggests that it could play the role of a catalyst or an accelerator in the oxidation reaction.

From the results obtained we can classify the oxidation power of the various systems studied as follows: TBAP \geq air in the presence of dodecanol-1 $>$ TBAP + air $>$ air. Increasing the "surface tension" is in accord with spectroscopic data and ESCA analysis (Table II and IV). Figure 4 shows an increase of the polar groups as measured by FTIR vs time (h).

The IR spectra of OPP oxidized by air shows an absorption band at $1690\text{--}1600\text{ cm}^{-1}$ of carboxylic acid groups^{25,26} and ethylenic double bonds and also H bonding at 3469 cm^{-1} .

In the case of the IR spectra, we can see the effect of the experimental conditions on the IR peaks (Table IV).

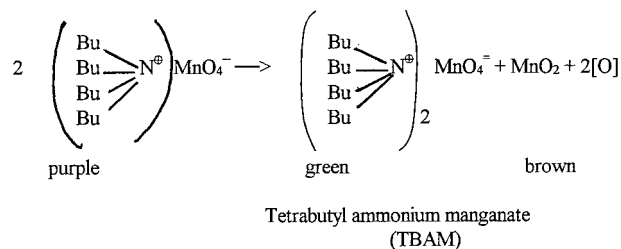
The percentage of polar groups as well as the hydrogen intermolecular bond at $3600\text{--}3100\text{ cm}^{-1}$ increases almost linearly with oxidation time (Fig. 4).

The iodometric test indicates that there is no measurable amount of hydroperoxides in OPP. Generally, these groups will decompose at approximately 130°C , which is our reaction temperature.^{27,28}

Proposed Reaction Mechanism

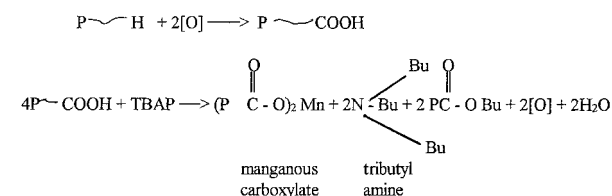
It has been shown that MnO_2 was formed and that polar groups were determined by IR, ESCA, and chemical methods. Furthermore, during the reaction, the purple solution of TBAP turned yellow-green and then yellow-brown and finally colorless with a suspension of brown MnO_2 particles. This suggests that we have decomposition of the permanganate to a manganate (green), i.e., from MnO_4^- to MnO_4^{2-} and finally to MnO_2 .¹⁸

From these results one could have the following reaction mechanism.

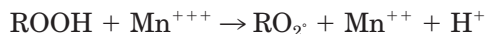


In the case of the oxidation by the TBAP, the pH of the solution increases to 8 which indicates the effect of an amine in the reacting medium.

ESCA analysis shows that 1.3% of the atoms in the oxidized PP by TBAP are Mn. This with the displacement of the IR absorption band at 1641 cm^{-1} when put in contact with HCl suggests the following mechanism^{6,29-31}:



Ions of heavy metals such as Mn^{+7} play the role of accelerator in the oxidation of olefins through the formation of an intermediary products such as $ROOMnA_2$.³²



The formation of ketone, ester, and acid groups by hydrocarbon oxidation can now be generalized. During the oxidation reaction with TBAP, the permanganate is initially converted to manganate and then to MnO_2 , creating atomic oxygens as oxidizing agent.

The efficacy of TBAP as oxidizer is higher than for the other oxidizing agents. The solubility of OPP in MEK may reach up to 10% W/W.

CONCLUSION

It has been shown that the oxidation of PP in the presence of air and TBAP creates oxygen containing polar groups such as ketones, anhydrides, or γ -lactones on the polymer chain. The presence of traces of dodecanol-1, as an accelerator, leads to the formation of keto-esteric groups, whereas in its absence, carboxylic acid groups and ethylenic double bonds are formed. The TBAP system favors the reaction towards the formation of carboxylic acids and salts of Mn. In all cases, only solid MnO_2 remains at the end of the reaction and is dispersed in the reacting medium.

The TBAP used for the oxidation reaction described herein was prepared in our laboratory, giving a conversion yield of over 99%.

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