Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

OXIDATION OF POLYPROPYLENE HOMOPOLYMER IN THE MOLTEN STATE IN PRESENCE OF AIR

Majid Abdouss[a]; Nasser Sharifi-Sanjani[a]; Pierre Bataille[b]
[a] Chemistry Department, University of Tehran, Tehran, Iran [b] Chemical Engineering Department, École Polytechnique, Montréal, Canada

To cite this Article Abdouss, Majid , Sharifi-Sanjani, Nasser and Bataille, Pierre(1999) 'OXIDATION OF POLYPROPYLENE HOMOPOLYMER IN THE MOLTEN STATE IN PRESENCE OF AIR', Journal of Macromolecular Science, Part A, 36: 10, 1521 — 1535

To link to this Article: DOI: 10.1081/MA-100101612

URL: http://dx.doi.org/10.1081/MA-100101612

J.M.S.—PURE APPL. CHEM., A36(10), pp. 1521–1535 (1999)

OXIDATION OF POLYPROPYLENE HOMOPOLYMER IN THE MOLTEN STATE IN PRESENCE OF AIR

Majid Abdouss and Nasser Sharifi-Sanjani

Chemistry Department
University of Tehran
Tehran, Iran

Pierre Bataille*

Chemical Engineering Department
École Polytechnique
P.O. Box 6079
succ. Centre-Ville
Montréal, Canada, H3C 3A7

Key Words: Oxidation, Dodecanol-1, Molten PP, Air

ABSTRACT

The oxidation of polypropylene (PP) homopolymer in air was performed using dodecanol-1 as an accelerator. The experiments were conducted under atmospheric pressure at 180-220°C. Spectroscopic data indicated the formation of polar groups such as ketones, esters, alcohols, anhydrides etc. as determined by FTIR and ESCA. The scanning electron microscopy (SEM) showed the variations of morphology of the oxidation products. The fusion temperatures were determined by differential scanning calorimetry (DSC). The variations of solubility of PPO as compared with the original PP were investigated in solvents such as MEK, THF, and toluene.

---

* Author to whom correspondence should be addressed.

www.dekker.com

Surface tension and molecular weights were determined by tensiometry and gel premeation chromatography (GPC). The melt flow index (MFI) of different samples were determined.

INTRODUCTION

The presence of tertiary carbons in isotactic polypropylene polymer matrix enhances greatly its oxidation possibilities [1-8]. The oxidation of polypropylene (PP) will change physical and mechanical properties of the polymer such as surface polarity, surface tension and adhesion of the polymer (9-14].

The effects of dilauryl thiodipropionate (DLTP), heptadecane and phenylbenzoate on oxidation of PP in presence of gossypol (a natural polyphenol: C_{30} H_{30} O_8) were studied [15-18]. DLTP increases the antioxidation effectiveness of gossypol, but heptadecane and phenyl benzoate have no effect on the reaction.

The photo and thermal oxidation of polypropylene with UV ray in the solid phase at different wavelengths (544 nm, 356 nm, etc…) were also studied [19-23].

The oxidation of PP in presence of Co(II), Co(III) ions [24-28], some peroxides and nitroxyl stable radicals [29] were also carried-out. The formation of polar groups such as alcohol, peroxide, ketone, anhydride, etc. was observed.

In this paper we present the results of oxidation of melted PP in presence of oxygen (air) and dodecanol-1 as an accelerator. The effects of temperature and time on the oxidation reaction were studied using an internal mixer.

EXPERIMENTAL

Material

The polypropylene powder without any additives of grade PIO105 was supplied by Himont Co., Varennes (Quebec), Moplen grade T30G.

The dodecanol-1 was obtained from Merck Chemical Co., Darmstadt, Germany. The solvents (MEK, toluene, THF and MeOH were all of analytical grade and also supplied by Merck Chemical Co.

Apparatus

The samples were characterized by FTIR-4300 (Shimadzu Co)., by scanning Electron Microscopy (SEM), (Cambridge Instrument; Stereo Scan 360), by gel permeation chromatography (GPC) (Waters 150-C) and by osmometry (V.P.O. Knauer). The surface tension of the polymer was determined by an automatic tensiometry (PROLABO). The melt flow index was measured using a MF1-592 of Motor Heizung. DSC measurements were obtained by using a DSC-7000 (ULVAC, Sinku-Riko).

Thermal analysis were conducted on a TA-7000 thermal analyzer basic component, analyzer (Dupont Co.). ESCA analysis were done on a Escalab 3 MK II).

The polymers were blended using a Brabender Plasti-Corder internal mixer PLE 331 of C. W. Brabender (South Hackensack).

Method

As indicated in Table 1, in the oxidation reaction of PP by air, first PP and dodecanol-1 were mixed in the internal mixer (Brabender). Dried and filtered air was then put in contact with the molten mass at a flow rate of 1L/min.

The reaction was conducted at temperature between 180-220°C for 2 1/2–6-1/2 hours.

Purification of Oxidized PP (PPO)

Oxidized PP was first dissolved in toluene (at 40-50°C) and then precipitated by pouring the solution in boiling methanol, after which it was filtered.

The white particles of polymer were washed with warm methanol (30°C) and dried under vacuum at room temperature. The recovered polymer corre-

TABLE 1. Oxidation Conditions of Polypropylene[a, b]

Trial Number	PP (g)	Oxygen (air) Flow rate (L/min)	Temperature (°C)	Reaction Time (hours)	Other Conditions
Reference	37	---	200	4	Pure N_2 only
1	38	1	180	2 ½, 4 ½, 6 ½	Pure N_2 only
2	38	1	200	2 ½, 4 ½, 6 ½	Pure N_2 only
3	38	1	220	2 ½, 4 ½, 6 ½	Pure N_2 only

a) Brabender mixer rotation speed of 60 RPM.
b) Presence of 100 mg of dodecanol-1

sponded to 83% of the original PP. About 9% of this oxidized PP stayed in the methanol-toluene solution indicating the high polarity of PPO.

RESULTS AND DISCUSSION

In the oxidation reaction of PP homopolymer, in oxygen (air) and trace amounts of dodecanol-1 produces interesting products, which can be used as wax or as compatibilizer in certain applications.

Solubility of Oxidized PP (PPO)

The results of the solubility of oxidized PP are given in Table 2. By increasing the reaction temperature the solubility of PPO in warm MEK and in THF will increase by up to 100%. These suggest a gradual increase of absorbed oxygen and by consequence an increase in the polarity of the PPO.

At room temperature all oxidized samples are soluble in toluene confirming this increase in the PPO polarity.

Spectroscopy Study

FTIR spectra of oxidized PP by air showed sharp bands at 3448, 1766, 1714, and 1163 cm^{-1} regions. The absorption band at 3448 cm^{-1} was attributed to the stretching mode of hydrogen bonded hyroxyl group in alcohols. The iodometric test indicated that there was no measurable amount of hydroperoxides in PPO. The stretching mode at 1766 cm^{-1} is attributed to anhydride carbonyl groups (see Figure 1 and Table 3).

TABLE 2. Solubility of Oxidized PP (PPO) in Warm MEK, THF and Cold Toluene

Polymer	Oxidation Agent	Oxidation Temperature (°C)	Oxidation reaction Time (h)	Solubility %		
				THF	MEK	Toluene
PP	None	---	---	0	0	---
PPO	0_2 (air)	180	6 ½	80	90	100
PPO	0_2 (air)	200	6 ½	80	95	100
PPO	0_2 (air)	220	6 ½	100	100	100

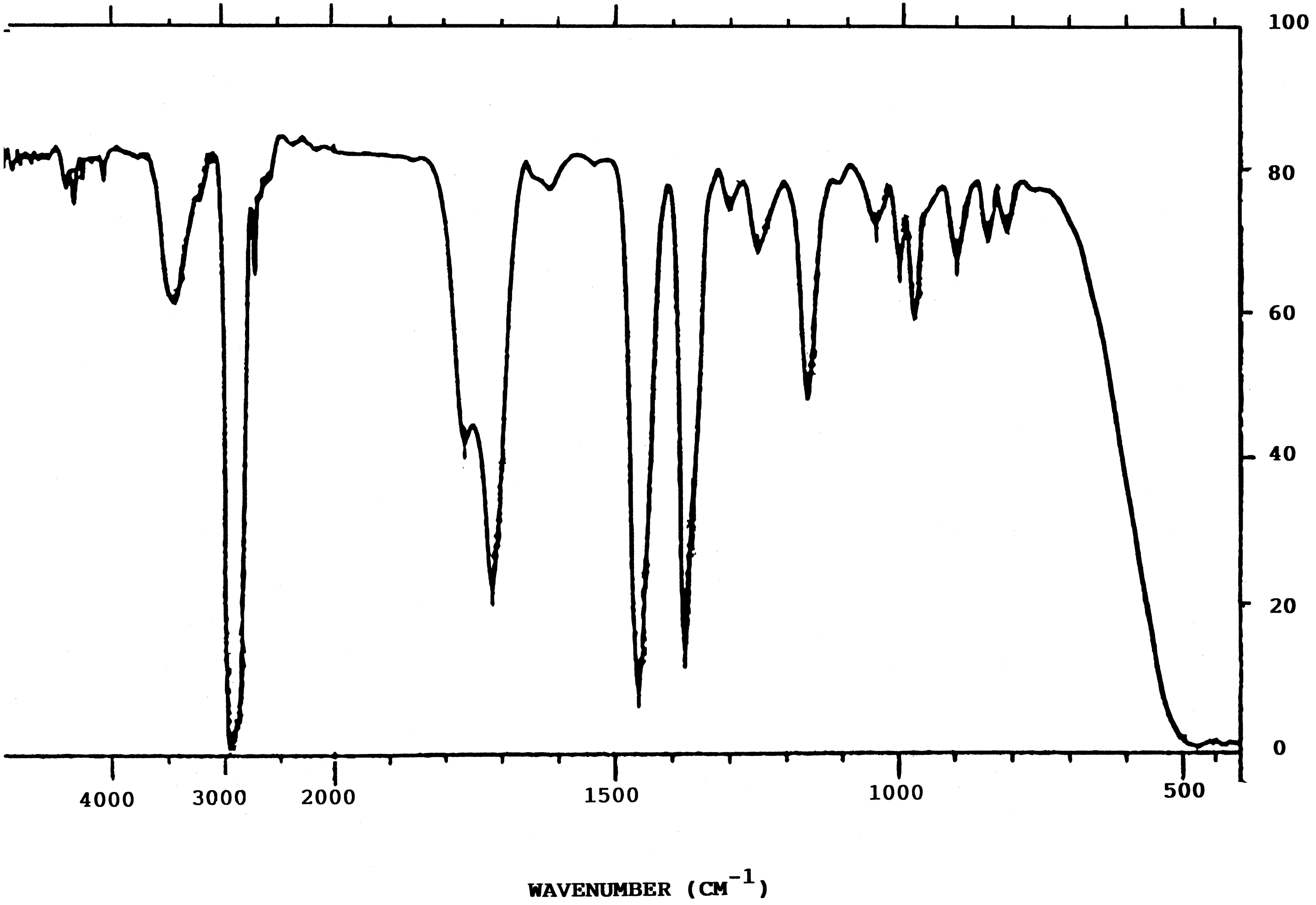


Figure 1. FTIR Spectra of Oxidized PP at 220°C.

TABLE 3. Oxidation Product of Polypropylene

Oxidation products	IR Band Frequency (cm^{-1})
Alcohol hydroxides	~ 3440
Ketone and aldehyde carbonyl	1719-1711
Anhydride carbonyl	1778-1775

Table 3 shows the products of oxidation of PP in presence of oxygen (air). The absorption bands ratios of polar groups and methyl was measured by FTIR (Table 4). By increasing the reaction temperature and time it increase the polar group concentration. These results were confirmed by ESCA (Table 5).

From the FTIR Spectrum no absorption bands of oxygenated groups was observed and it is only after 6-1/2 hours of mixing that a very weak band appears. The ratio between the absorption bands of 1800-1668 cm^{-1}/1377 cm^{-1} is about 0.0013, whereas it is 0.469 for PPO in the same conditions but in the presence of dodecanol-1.

TABLE 4. Absorption Bands Ratios Between the Carbonyl Groups from Ketones, or Anhydride and Methyl Groups

Polymer	Temperature (°C)	Mixing Time (hours)	Ratio between the Absorption Bands 1800-1668/1377
PPO	180	2 1/2	0.2422
PPO	180	4 1/2	0.3436
PPO	180	6 1/2	0.4660
PPO	200	2 1/2	0.2092
PPO	200	4 1/2	0.3731
PPO	200	6 1/2	0.4692
PPO	220	2 1/2	0.3500
PPO	220	4 1/2	0.7339
PPO	220	6 1/2	2.0796

TABLE 5. Percentage of Oxygen in PPO (ESCA Analysis)

TEMPERATURE	180°C	200°C	220°C
O_{1s}	6.06	6.33	6.72
C_{1s}	93.94	93.67	93.28
$^*O_{1s}$		0.6	

*in absence of dodecanol-1.

Esca Analysis

The percentages of oxygen in PPO at different temperatures (180, 200 and 220°C) for 6-1/2 hours are given in Table 5. According to ESCA measurements, the percentage of oxygen absorbed by polymer increases with temperature. This analysis confirmed the solubility and FTIR experiments results.

Surface Tension

The surface tension of PPO was measured in toluene. The surface tension of PP was 30.01 dyne/cm after oxidation at 180, 200 and 220°C, it increases, respectively to 32.10, 33.08, and 34.51 dyne/cm (see Figure 2). The increasing of percentage of oxygen or "surface tension" is in accord with spectro-scopic data and ESCA analysis (Tables 4 and 5).

The ESCA analysis shows 0.6% of oxygen in the PPO-(Table 5) but when the mixing is done in presence of dodecanol-1, it rises to 6.33% of more than 10 times again the original amount. Furthermore, the PPO obtained in presence of dodecanol-1 is soluble at 80% in THF, 90% in MEK and 100% in Toluene as compared to respectively to 4% in THF, 6.5% in MEK and 8% when the PP is oxidized in absence of dodecanol-1. From these FTIR, ESCA and solubility results, it can be seen that the dodecanol-1 plays an important role as accelerator or oxidation catalyst with PP. These results are similar to the ones obtained with PP in a solution of monochlorobenzene [30].

Molecular Mass and Molecular Mass Distribution

Oxygen (air) is a strong oxidant for PP in a molten state. The percentage of oxidation is so high that the oxidized PP at 220°C during 6-1/2 hours is completely soluble in solvents such as toluene, MEK and THF (Table 2). Molecular mass was determined by GPC with THF as solvent and also by VPO. The results

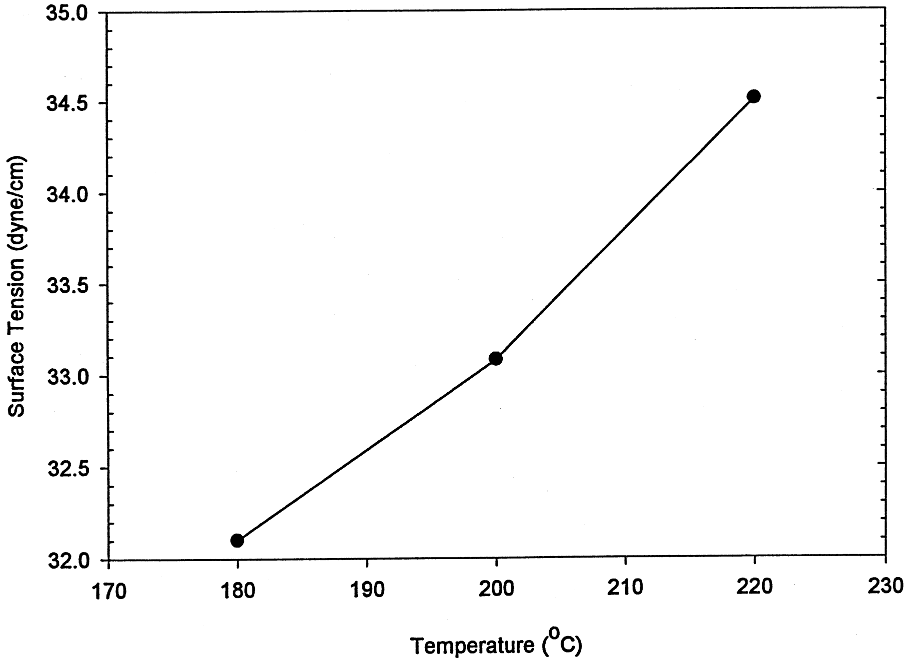


Figure 2. Surface Tension (dyne/cm) vs. Temperature (°C).

of GPC were calculated using area normalization [w(t)] and molecular weight normalization [W(t)/-d(logM_w)/dt].

This gave a $\overline{M}_w$ of 6014, a $\overline{M}_n$ of 1686 with a molecular mass distribution 3.5.

The oxidized samples at 180°C and 200°C weren't completely soluble in THF (about 80% solubility in THF). Thus, we had to use the osmometry V.P.O. method for determining molecular mass. The solvent used was toluene, the experiment was run at 75°C for 3 minutes for each measurement. The calibrating solution was Benzyle.

The comparison and variation of $\overline{M}_n$, MFI and fusion temperature for PPO in 6-1/2 hours is shown in Table 6 and Figure 3. The results of Tables 4, 7, and Figure 3 show that by increasing temperature, the percentage of oxygen absorption, MFI, surface tension and polarity of the macromolecule chain will increase. On the other hand structural variations due to formation of new chemical groups is increased, and scission of covalent bonds is facilitated. Consequently molecular weights and fusion points decrease, but MFI increases.

TABLE 6. Compararison MFI and fusion temperature for PPO in 6-1/2 hours

Polymer	Oxidation Temperature(°C)	$\overline{Mn}$ (GPC)*	$\overline{Mn}$ (V.P.O)	MFI (105°C/1.2 kg) (g/10 min)	DSC F.P. (°C)
PP	---	---	181000	1.50**	168.15
PPO	180	---	4565	4.32	137.40
PPO	200	---	4385	7.42	122.80
PPO	220	1694	---	9.40	113.20

* $\overline{M}_w$: 6014, $\overline{M}_w$D : 3.5

**at 190°C/2.16 kg (g/10 min)

Scanning Electron Microscopy (SEM)

The SEM was used to study the morphology of the polymer. In Figure 4 is given the SEM analysis of variances samples of PP, it showed that the surface of the unoxidized polypropylene was smooth, whereas the oxidized samples showed a granulated structure. On the surface of oxidized PP of “bumps” and “craters” are observed. By increasing the percentage of the absorption of oxygen, there is an increase in “bumps” and “craters”.

Thermal Analysis (DSC)

The oxidized samples were scanned between 25-250°C, at an heating rate of 10°C/min and a chart speed of 15 mm/min. The results are given in Table 7.

Furthermore, the results in Tables 6 and 7 showed a permanent decrease of fusion points and molecular mass with the appearance of new peaks. These results correlate with the molecular weight measurements by GPC and by V.P.O.

Proposed Reaction Mechanism

The results of FTIR, ESCA indicated the presence of polar groups such as ketones, alcohol’s and anhydrides.

Some of the suggested mechanisms are given elsewhere [31, 32]. As for the role of dodecanol-1, nothing specific was published. But from our experience, after purification of PPO i.e. precipitation of PPO in methanol and evaporation a small amount of residue was found. This residue has a fusion point of 23 ± 1°C and a boiling point of 255 ± 1°C, which corresponds exactly to the phys-

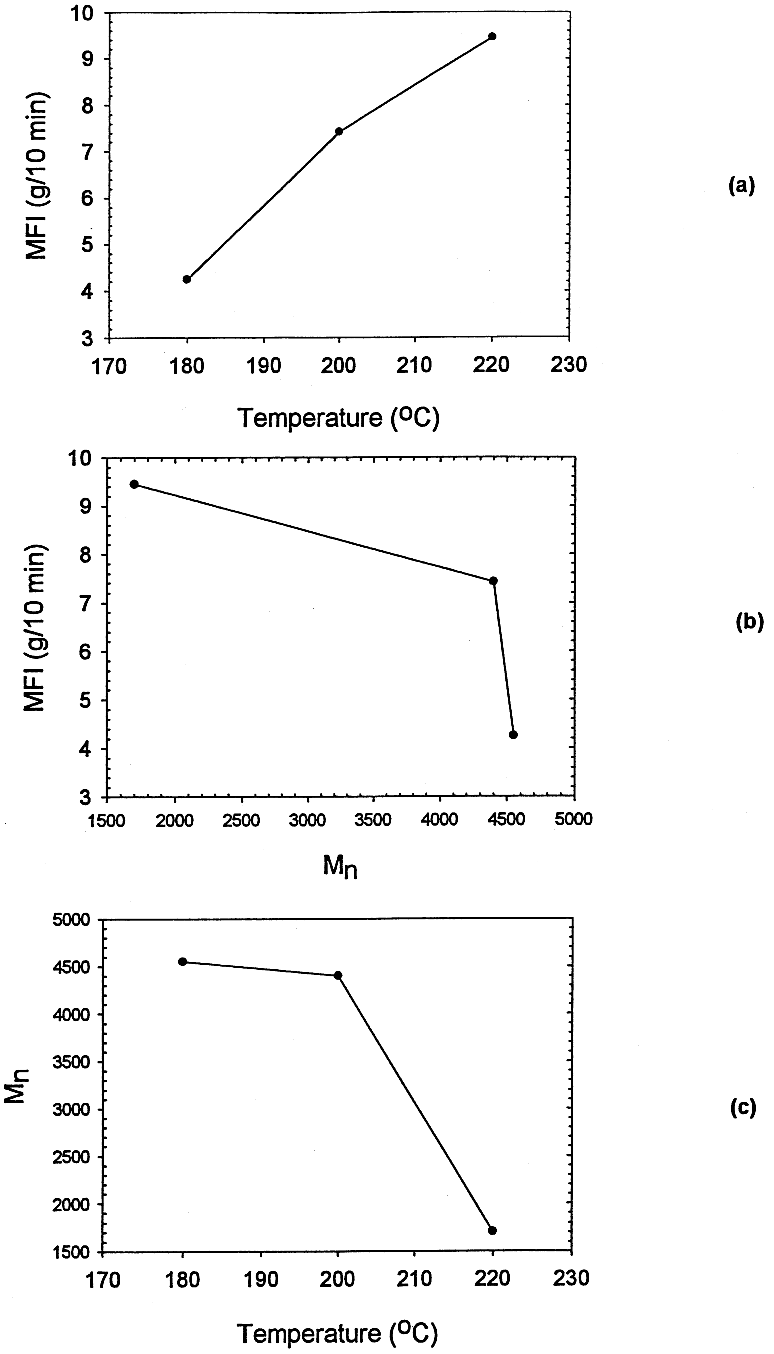


Figure 3. (a) MFI (g/10 min) vs. temperature (°C).(b) MFI (g/10 min) vs. $\overline{M}_n$. (c) vs. temperature (°C).

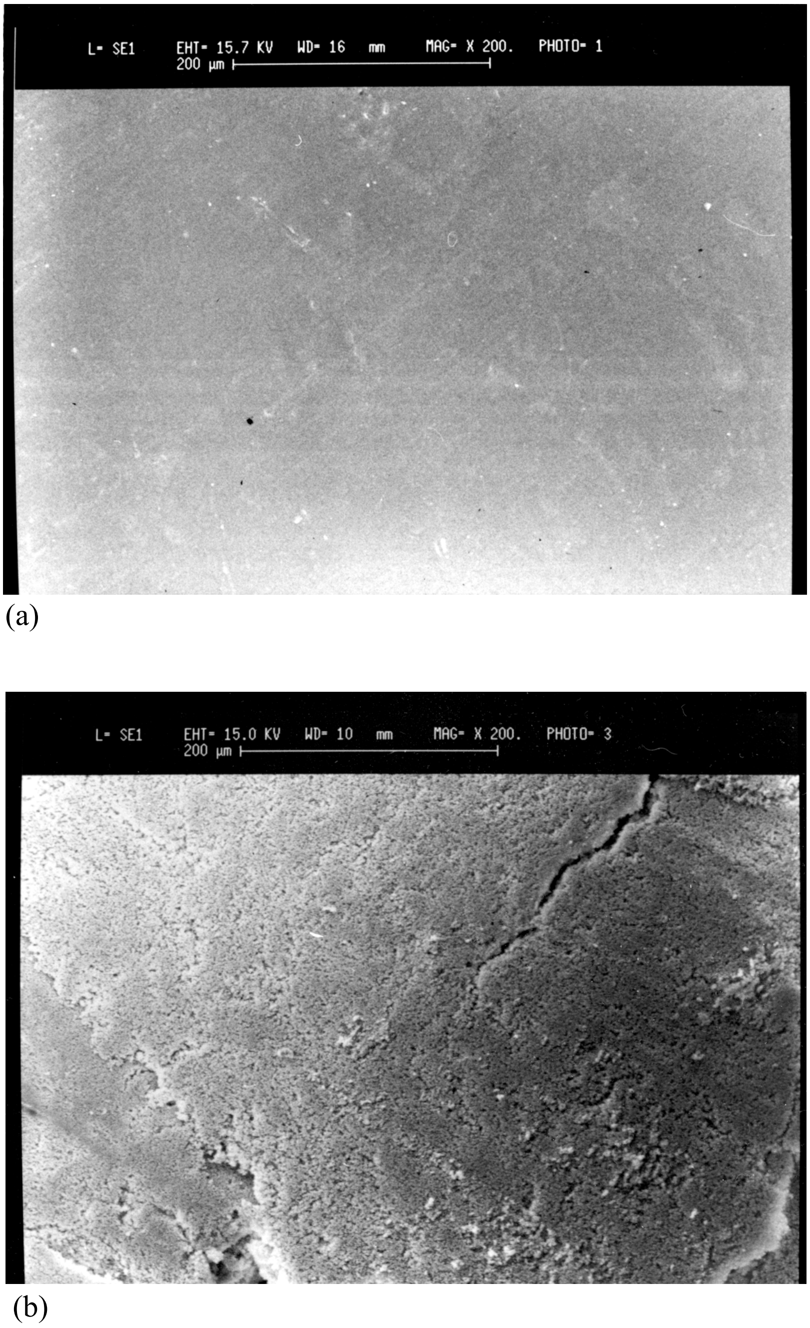


Figure 4. Scanning Electron Microscope Results: (a) Unoxidized PP. (b) Oxidized PP at 220°C for 4-1/2 hours. (c) Oxidized PP at 220°C for 6-1/2 hours. (d) Oxidized PP at 200°C for 6-1/2 hours. (e) Oxidized PP at 180°C for 6-1/2 hours.

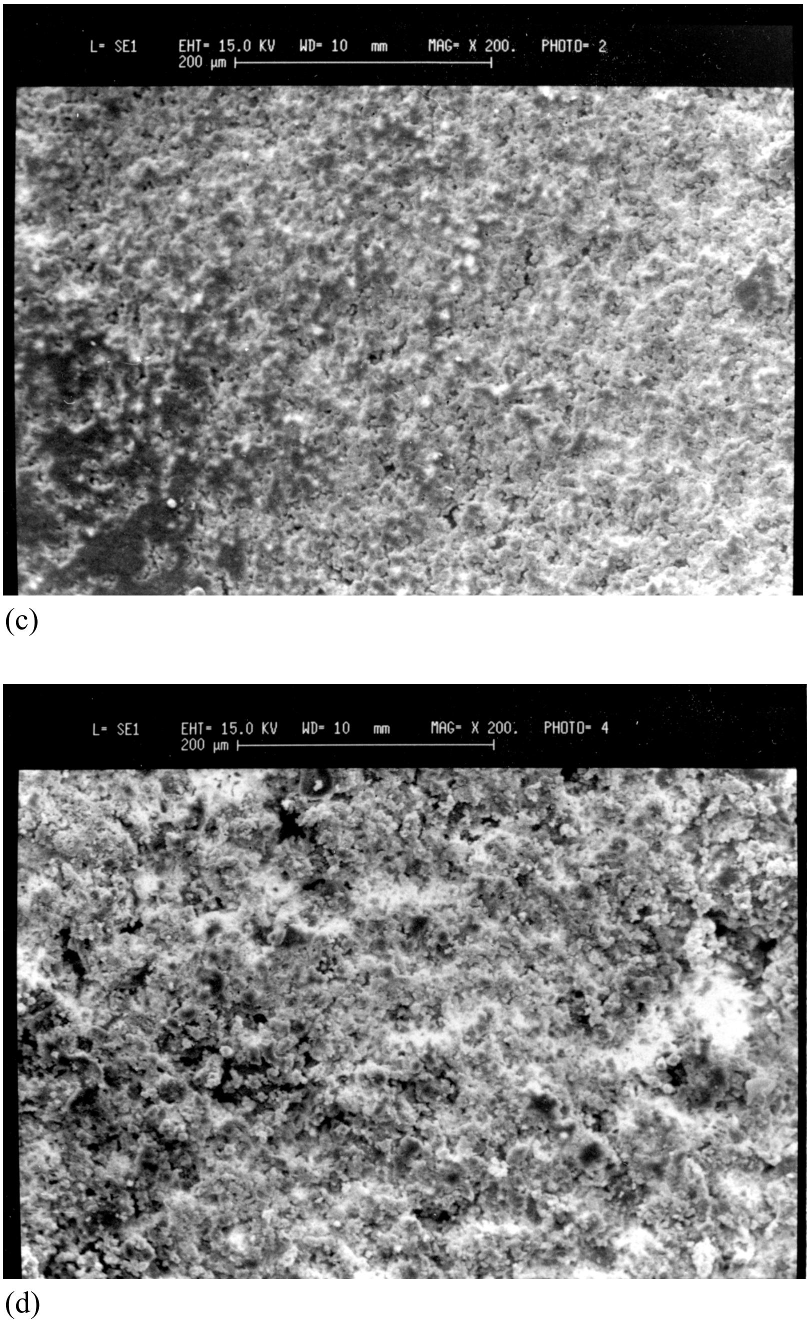
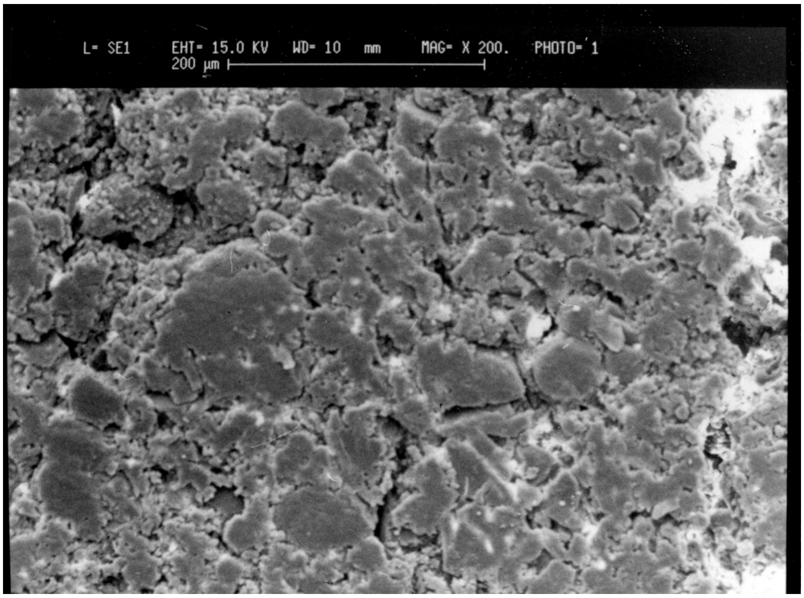


Figure 4. Continued.



(e)

Figure 4. Continued.

ical properties of dodecanol-1. This suggests that the dodecanol-1 was not part, as such, of the final product but played a role as an accelerator or as a catalyst.

It is known that dodecanol-1 plays a role as an external lubricant for PP and it has a preferential interaction with free radicals generated by the thermal degradation of the polymer matrix. This will permit the free radicals which are

TABLE 7. Thermal Analysis Results (DSC)

Polymer	Oxidation Temperature (^oC)	Oxidation Reaction time (hours)	Fusion Temperature (^oC)	Fusion Point (^oC)
PP	---	---	168.15	---
PPO	180	4 1/2	139.05	129.3
PPO	180	6 1/2	137.40	---
PPO	200	4 1/2	142.20	113.4
PPO	200	6 1/2	122.80	---
PPO	220	4 1/2	133.10	94.4
PPO	220	6 1/2	113.20	78.4

inside the polymer structure to migrate to the surface favoring the oxidation reaction in presence of oxygen.

CONCLUSION

The oxidation of PP homopolymer in the presence of air and trace amounts of dodecanol-1 resulted in the formation of polar groups such as ketones, esters, alcohols, anhydrides etc. The reaction was greatly enhanced as compared to the case when the dodecanol is absent. The amount of absorbed oxygen, surface tension, MFI and solubility in polar and toluene solvents will increase with the temperature and oxidation reaction time. The oxidized samples of PP are completely soluble in toluene at room temperature, but 90-100% in warm MEK and 80-100% in warm THF. Meanwhile molecular weight and fusion point decrease. The surface morphology of the polypropylene is greatly affected by the oxidation conditions with the appearance of “bumps” and “craters” on the polymer surface.

ACKNOWLEDGEMENT

The authors gratefully acknowledge support from the Committee of Research Affairs of the University of Tehran, from the NPC of Iran and from the Natural Sciences and Engineering Research Council of Canada.

REFERENCES

[1] B. L. Goodall, *J. Chem. Educ., 63*, 191 (1986).

[2] A. Hoff and S. Jacobsson, *J. Appl. Polym. Sci., 29*, 465 (1984).

[3] M. Iring, S. Laszlo-Hedvig, K. Barbos, and F. Tüdos, *Eur. Poly. J., 14,* 439 (1978).

[4] Toyota Motor Co; Ltd. JP 57, 156 365, sept. 27, 1982.

[5] M. Fujiyama and H. Awaya, *J. Appl. Polym. Sci., 16*, 275 (1972).

[6] A. R. Padel, A. D. Dibattista, and P. P. Klemchuk, *J. Appl. Polym. Sci., 16*, 2751 (1972).

[7] E. Niki, C. Decker, and F. R. Mayo, *J. Polym. Sci.; Polym. Chem. Ed., 11,* 2813 (1973).

[8] O. Yaykin and O. T. Savasci, *J. Appl. Polym. Sci., 37(8),* 2383 (1989).

[9] D. J. Carlsson, R. Brousseau, and D. M. Wiles, *Polmer Degrad. Stab., 15,* 67 (1986).

[10] A. Garton, D. J. Carlsson, and D. M. Wiles, *Dev. Polym. Photochem 1*, 93 (1980).

[11] T. J. Henman, *Dev. Polym. Stab., 6*, 107 (1985).

[12] D. Briggs and C. R. Kendall, *Int. J. Adhesion, 13*, 199 (1982).

[13] R. J. Pace and A. Datyner, *J. Polym. Sci., Polym. Phys. Ed. 18*, 1103 (1980).

[14] Y. A. Shlyapnikov and A. P. Marin, *Eur. Polym. J., 23*, 629 (1987).

[15] A. P. Marin, Yu A. Shlyapnikov, E. S. Mametov, and A. T. Dzhalilove, *Polymer Degrad. Stab., 35,* 229 (1992).

[16] A. R. Assink, *J. Polym. Sci., Polym. Phys. Ed., 13*, 1665 (1975).

[17] R. M. Barrer and J. M. Barrie, *J. Polym. Sci., 23*, 331 (1957).

[18] Y. A. Shlyapnikov, *Macromol. Chem., Macromol. Symp., 27*, 121 (1989).

[19] Q. Yang and K. Martin, *J. Appl. Polym. Sci., 51*, 389 (1994).

[20] A. Horrocks and J. A. Dsouza, *J. Appl. Polym. Sci., 42*, 243 (1991).

[21] A. R. Horrocks and J. A. Dsouza, *Thermochim. Acta, 134*, 255 (1988).

[22] G. Steiner and J. Koppelmann, *Polym. Deg. Stabil., 19,* 307 (1987).

[23] C. R. Boss and J. C. W. Chien, *J. Polym. Sci., A-1, 4,* 1543 (1966).

[24] G. C. Furneaux, K. J. Ledbury, and A. Davis, *Polym. Degrad. Stab., 3,* 431 (1981).

[25] L. Taimr and J. Pospisil, *Angew. Makromol. Chem., 52,* 31 (1976).

[26] L. Taimr, M. Pivcova, and J. Pospisil, *Collect. Czech. Chem. Commun. 37,* 1912 (1972).

[27] J. Kovarova-Lerchova and J. Pospisil, *Eur. Polym. J., 13*, 975 (1977).

[28] J. Kovarova-Lerchova and J. Pospisil, *Eur. Polym. J., 14 (7),* 463 (1978).

[29] V. A. Roginskii and V. B. Miller, *Vysokomol. Soedin, Ser. B. 21(7*), 521 (1979).

[30] M. Abdouss, N. Sharifi-Sanjani, and P. Bataille, Paper submitted for publication.

[31] A. Bravo and J. H. Hotchkiss, *J. Appl. Polym. Sci., 47*, 1741 (1993).

[32] P. Gijsman and J. Hennekens, *Polym. Degrad. Stabil., 42,* 95 (1993).

Received June 25, 1998
Revision received June 1, 1999