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Valuable oxygenates by aerobic oxidation of polymers using metal/bromide homogeneous catalysts

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Abstract

A method of plastics recycling by selectively oxidizing 10 different polymers is demonstrated using homogeneous, liquid phase aerobic oxidation in acetic acid with metal/bromide catalysts and in water using vanadium/bromide catalysts. Some examples are the conversion of polystyrene to benzoic acid in 88% yield, polypropylene to acetic acid in 63% yield, polylethylene to a mixture of succinic, glutaric, and adipic acid in 47% yield, poly(butylene)terephthalic acid to terephthalic acid and succinic acid, the latter in 37% yield, and poly(vinyl)chloride to succinic acid in 38% yield.

Keywords: Valuable oxygenates; Aerobic oxidation; Homogeneous catalysts

1. Introduction

The first *synthetic* polymer, celluloid nitrate from cotton and nitric acid, was invented in 1868 and was followed in the next 100 years with the invention of 64 distinct industrial polymers having a volume of over 140 billion lb per year (BPY) [1]. The ecological disposal of plastics has therefore been a major concern and many methods have been proposed to solve it including using polymers as feedstocks to produce simpler chemicals [1–3]. Unfortunately direct recycling nearly always produces a quality poorer than the virgin material due to the exposure of plastics to air, heat, sun and water during their lifetime and to the recycling process itself. Most polymers are exposed to an air atmosphere consisting of 20.9% dioxygen (molecular oxygen, O_2) in the presence of ultraviolet light, which can act as a free radical initiator. Hence a slow autoxidative degradation of polymers occurs with the formation of hydroperoxides, carbonyl, and carboxylic acid derivatives on the surface. This process has been described in numerous scientific studies [4]. What if one *purposely* continued this oxidation process? In general, could valuable chemicals (B, C, D, etc.) be generated by such a methodology?

$$[A]_n + O_2 \overset{\text{homogeneous catalyst}}{\underset{\text{solvent}}{\rightarrow}} B + C + D + \cdots + H_2O \quad (1)$$

This approach is in contrast with the total oxidative combustion of used plastics (pyrolysis) ($[A]_n \rightarrow CO + CO_2$) or wet air oxidation [5,6].

We report here the direct aerobic oxidation of the five largest volume polymers—polyethylene (PE, world production 61 BPY in 1990), poly(vinyl)chloride (PVC, 36 BPY), polystyrene (PS, 20 BPY), polypropylene (PP, 12 BPY), poly(ethylene)terephthalate (PET,

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10 BPY) [1]—as well as some selected polymers where useful oxygenates could be postulated. Among the available homogeneous autoxidation catalysts [7,8], the catalysts chosen here are the metal/bromide combinations that have revolutionized the manufacture of aromatic acids [8]. The highly active and selective Co/Mn/Br and Co/Mn/Zr/Br combinations in carboxylic acid solvents [8,9] are used industrially to produce such acids as terephthalic acid from *p*-xylene, isophthalic acid from *m*-xylene, trimellitic acid from 1,2,4-trimethylbenzene (pseudocumene) and 2,6-naphthalenedicarboxylic acid from 2,6-dimethylnaphthalene.

Photo- and thermal degradation of polyethylene has produced very low yields of dicarboxylic acids and ketoacids [10]. The approach used here is similar to that recently reported by Sen and co-workers where polyethylene has been oxidized using nitrogen oxide and dioxygen to aliphatic di-acids and polystyrene to benzoic acid [11,12]. The presence of nitrogen oxide does produce nitro-derivatives such as nitrobenzoic acid. The methodology could not be applied to PVC or condensation polymers such as PET. The homogeneous oxidation of polypropylene using a Co catalyst in acetic acid has been reported to yield resinous materials having molecular weights of 250–730. No acetic acid was observed in this study [13]. Autoxidation of PVC in strong NaOH aqueous solutions yields oxalic and benzenecarboxylic acids [14]. The homogeneous Co/Mn/Br catalyzed co-oxidation of PET and *p*-xylene in acetic acid to obtain polyester-quality terephthalic acid has been reported [15].

2. Experimental

2.1. Description and characterization of polymers used

All polymers were used as received. Aldrich poly(vinyl)chloride was a fine powder with an inherent viscosity of 1.26, density of 1.385 and a molecular weight of 300,000. Aldrich polystyrene pellets had a density 1.047 and average M_w = 280,000. Aldrich polypropylene had a average M_w = 12,000, average M_n = 5000, and viscosity = 6.0 P at 190 °C. Aldrich poly(2-vinylpyridine-co-styrene) was granular with an average M_w = 220,000 having a styrene content of 30% Aldrich poly(4-vinylpyridine) was 2% cross linked. Translucent, clear pellets of Aldrich poly(bisphenol A)carbonate had a melt index of 7. Aldrich polyethylene was a fine powder with mp 109–111 °C, d = 0.940. Polyethylene(naphthanate) was DuPont Kaladex® film, 1000/340 gauge. Poly(ethylene)terephthalate was ground, recycled bottle resin from Reprise Technology, EVC Compounds Ltd., Cheshire, UK.

^{13}C-NMR analysis of the PVC in 1,2,4-trichlorobenzene indicated that the polymer was atactic with no trace of impurities or plasticizers. The syndiotactic (rr), heterotactic (rm), and isotactic (mm) ratios were 33, 49, and 19%, respectively. Similarly the PS was predominantly atactic with a trace impurity at 30 ppm which may be PE or grease. The polypropylene is primarily isotactic with a tacticity ratio of mm = 86.5, mr = 6.6, rr = 6.9%. The polyethylene is a low density PE. The type of branches is given in Table 6. There was an unidentified additive in the PE of about 0.7 mol%.

2.2. Catalyst preparation

The catalysts were prepared by dissolving the metal salts in the given solvent. Cobalt(II), manganese(II), cerium(III), and Ni(II) were the metal acetate hydrates and used as received. Aldrich zirconium(IV) acetate solution, Baker ammonium metavanadate and EM Science sodium bromide were used as received.

2.3. Oxidation of polymers

The oxidation experiments were typically performed as follows: 0.2–0.5 g of polymer, weighed to 0.0001 g was placed in 5.2 g of a solution containing the catalyst and solvent in a 20 cc agitated glass reactor. The reactor was pressurized at 70 bar in air. *Caution: the use of high pressures and the use of dioxygen/nitrogen mixtures are potentially explosive and dangerous. They should be performed only with adequate barriers for protection.* The reactor was heated to the specified temperature and subsequently held at this temperature for the specified amount of time. The time to heat the reactor to the specified temperature was about 15 min. The reactor was then cooled to room temperature (requiring about 1 h),

while still under air, the system de-pressurized and its contents analyzed via liquid (LC) and gas chromatography (GC).

An HP6890 Gas Chromatograph equipped with a FID detector was used to identify the reaction products. The column was a 25 m HP-FFAP with 0.32 mm i.d. and 0.5 μm film thickness. The initial temperature is 50 °C for 5 min. The GC is then ramped at 5 °C/min to 220 °C and held for 1 min at that temperature.

The white solids obtained after the oxidation of poly(ethylene)terephthalate (PET), poly(butylene) terephthalate (PBT), and poly(ethylene)naphthanate (PEN) were filtered, washed with 10% water/acetic acid to remove residual paramagnetic catalyst metals, air dried, weighed, and then analyzed via NMR by dissolution in deutero-dimethylsulfoxide. The determination of the oligomer present in the solids was obtained from the NMR spectra from the integrated area at 4.5 tau units (methylenic protons of the ethylene glycol) and that of terephthalic acid by the integrated area at 8.0 tau units (aromatic ring protons). Yields to terephthalic acid and 2,6-naphthalenedicarboxylic acid were determined by the weight of the isolated dried solids, after correction of the presence of the oligomer, since these acids are 99.9% insoluble in acetic acid/water solutions at room temperature [8]. PET itself is virtually insoluble in dimethylsulfoxide. There is considerable error in these yields since only 0.20 g of initial polymer was used in each experiment, resulting in a maximum of only 0.15 g of terephthalic acid.

An example of the determination of the acetic acid yield from the autoxidation of polypropylene *in acetic acid as the solvent* was determined as follows: 0.4061 of polypropylene was oxidized in 5.6725 g of deutero-acetic acid using a Co/Mn/Br catalyst. The slurry was filtered and the filtrate distilled to give 4.422 g of distillate. 0.2017 of toluene was added to 1.0073 g of the distillate and the proton NMR measured. The yield of acetic acid was calculated from the integrated area of the toluene and the methyl resonance of acetic acid in the H-NMR.

2.4. GC/MS results on the products of reaction

GC/MS spectra were obtained directly on the filtrates. The filtrates were then evaporated to remove the acetic acid and the active hydrogens derivatized with Supelco Sylon BFT (a mixture of *N*,*O*-bis (trimethylsilyl)trifluoroacetamide and trimethylchlorosilane). A GC/MS was performed on the derivatized products.

Autoxidation of polyethylene using Co/Mn/Br catalyst in acetic acid—dominant peaks are $HOOC(CH_n)COOH$ with $n = 2$, 3, and 4 (succinic, glutaric, and adipic acids) with much smaller amounts of $n = 5$ and 6 (pimelic and suberic). Also present in small amounts are 1,4-dicarboxy-1-butene, propionic acid, butanoic acid, butyrolactone, and 2,5-furandicarboxylic acid. The normal acetic acid decomposition products are also seen—formic acid, glycolic acid, monobromoacetic acid, dibromoacetic acid, maleic acid, methyl acetate, and methanol.

Autoxidation of polystyrene gave the products shown in Fig. 1 as well as the acetic acid decomposition products (formic acid, methyl acetate, succinic, and maleic acid).

Autoxidation of polypropylene using a Co/Mn/Br catalyst in acetic acid produced small amounts of acetic acid decomposition products—methyl acetate, bromoacetic acid, and succinic acid. The autoxidation of PP in water using V/Br catalysts gave acetic acid as the predominant product followed by acetone. Methanol, formic acid, propionic acid, succinic acid, possibly 3-pentene-2-one ($M_w = 84$), and dimethymalonic acid ($M_w = 132$) were identified in small amounts.

Autoxidation of poly(vinyl)chloride using a Co/Mn/Br catalyst in acetic acid at 180 °C for 2 h gave mono- and dichloroacetic acid, acetoxyacetic acid, glycolic acid and formic acid as the predominant products. In addition small amounts of the usual acetic acid decomposition products are seen (monobromoacetic acid, methyl acetate, maleic (or fumaric acid), succinic acid). The GC/MS from the V/Br catalyzed oxidation of PVC in water gave only succinic acid.

Autoxidation of poly(bisphenol A)carbonate using a Co/Mn/Zr/Br catalyst in acetic acid gave 4-hydroxybenzoic acid as the major product along with the others shown in Fig. 2.

2.5. Solubility of the polymers in acetic acid

The solubility of the selected polymers were determined by refluxing them in acetic acid for

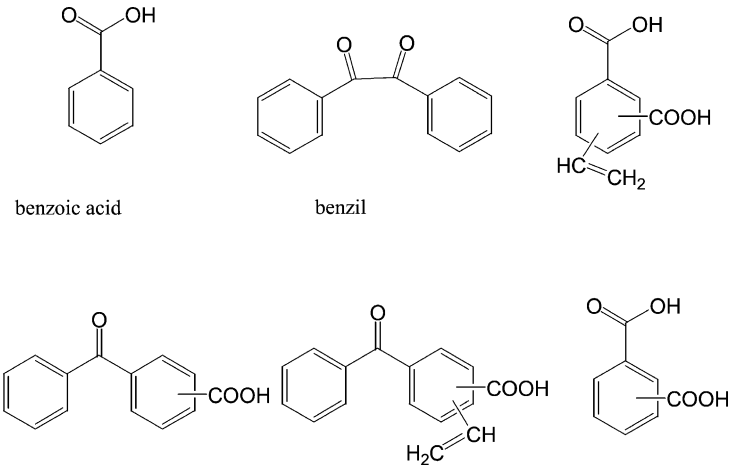

Fig. 1. Products identified via GC/MS from the autoxidation of polystyrene at 205 °C for 1 h using Co/Mn/Br catalyst.

5 h and filtering them while hot. Poly(carbonate), poly(ethylene)terephthalate, polypropylene, and poly-(vinyl)chloride had a 2.4, 5.3, 2.8, and 0.91% weight loss, respectively. Poly(4-vinylpyridine) and PC gained weight by 5.3 and 18% presumably due to influx of solvent into the polymer.

3. Results and discussion

3.1. General comments

The aerobic oxidation of polymers to simple monomeric chemicals is a complex process consisting

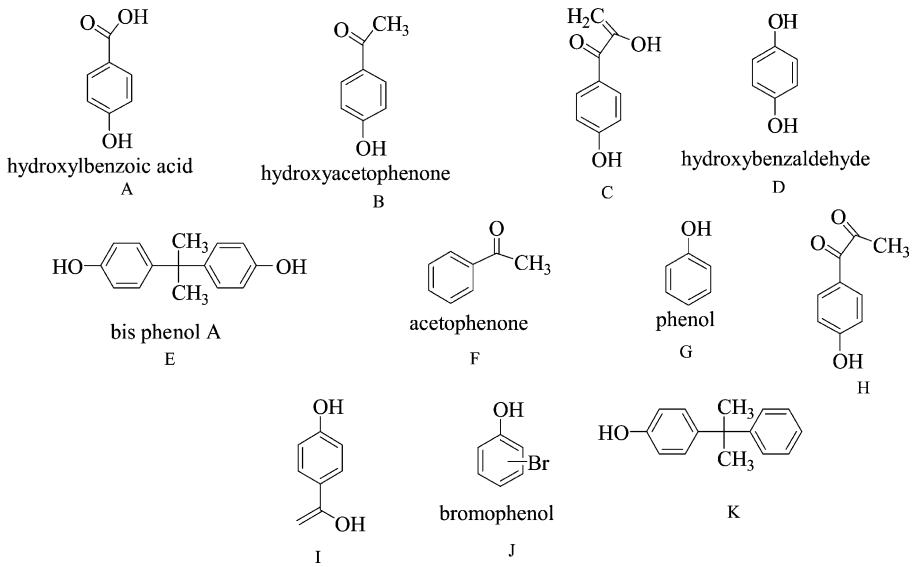

Fig. 2. Products identified via GC/MS from the autoxidation of poly(bisphenol A)carbonate using a Co/Mn/Zr/Br catalyst for 2 h at 180 °C in acetic acid.

of the reactions:

$$[\text{polymer}]_{\text{solid}} + O_2 \rightarrow [\text{oxidized polymer}]_{\text{solid}} \quad (2)$$

$$[\text{oxidized polymer}]_{\text{solid}} \rightarrow [\text{oxidized polymer fragment}]_{\text{solution}} \quad (3)$$

$$[\text{polymer}]_{\text{solid}} \rightarrow [\text{polymer}]_{\text{solution}} \quad (4)$$

$$[\text{polymer}]_{\text{solution}} + O_2 \rightarrow [\text{oxidized polymer fragment}]_{\text{solution}} \quad (5)$$

$$[\text{oxidized polymer fragment}]_{\text{solution}} + O_2 \rightarrow \text{stable monomeric product} \quad (6)$$

The oxidation reactions 2, 5, and 6 are highly spontaneous (*p*-xylene to terephthalic acid has a enthalpy change of −336 kcal/mol) and are essentially irreversible reactions. The stable monomeric product in reaction 5 will generally not be peroxides, alcohols and aldehydes since they rapidly oxidize to ketones and carboxylic acids. In general polymers are only 1–5% soluble after refluxing in acetic acid for 5 h (see Section 2) hence reaction 4 can be, and at least for polystyrene, is a limiting rate. The polymers may also congeal before dissolution and reduce their rate of reaction(s) by the decrease in surface area. Homogeneous liquid phase reactions have a large variable space—time, temperature, polymer concentration, type and composition of catalyst, catalyst concentration, oxygen pressure and type of solvent [8]. In general conditions have been found where satisfactory yields have been found. No attempt has been made however to explore this variable space to obtain optimum yields. Unless otherwise stated, yields may be limited by the incomplete reaction of the polymer due to insufficient rate of dissolution.

3.2. Autoxidation of polystyrene

The predominant products of polystyrene autoxidation are benzoic acid and benzil. Other by-products, deduced by GC/MS are given in Fig. 1.

Polystyrene was initially aerobically oxidized by passing air through an acetic acid solution in a well-stirred glass reactor containing the highly active Co/Mn/Zr/Br catalyst at 95 °C and ambient atmospheric pressure. The rate of oxygen uptake was 4.7×10^{-7} mol/s. At this rate, assuming a stoichiometric reaction of polystyrene to benzoic acid, the reaction would take approximately 72 h to complete. Solids were evident during the reaction and after 24 h, 85% of the initial weight of solid polystyrene was recovered. The initial clear pellets had congealed into a single spherical mass. Under comparable conditions, 1,2,4-trimethylbenzene with a Co/Mn/Br catalyst, which is completely soluble in acetic acid reacts at a rate of 6.6×10^{-6} mol/s or 14 times faster. The insolubility and changes in the physical state of the polystyrene are rate limiting. Raising the temperature to 180 °C for 2 h at 70 bar air, also resulted in slurry (see Table 1). Analysis of the filtrate gave a 26 (4)% molar yield to benzoic acid. ^{1}H-NMR analysis of the dried solids gave 87% polystyrene, 12% acetic acid with possibly 2% of oxidized material. Recovery of these spherical balls gave 52% of the original weight of the polystyrene added. When the reaction was extended to 5 h, no solids were present after reaction and the yield was 88 (2)%—close to quantitative yields. The yields obtained in this work of 88 mol% compare to that obtained using NO/O_2 mixtures of 26 mol% (at 17 h at 170 °C) [12]. Reported yields from various sources of benzoic acid from toluene using metal/bromide catalysts are 73, 86, 88, and 96% and from ethylbenzene 79, 79, 87, 90, and 96%; see [8].

The yields increase from 7–36 to 73 mol% as the temperature was increased from 150–180 to 220 °C, see Table 1. The lower yield at 220 °C than at 180 °C may be due to decarboxylation of the benzoic acid. A number of non-bromine catalysts were also evaluated using typical autoxidation catalysts metals—combinations of cobalt, manganese, cerium, nickel, zirconium—as well as the Co/*N*-hydroxyphthalimide

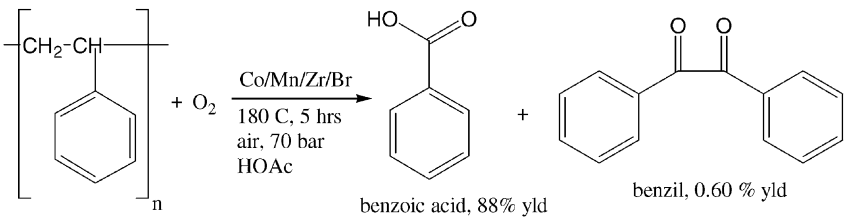

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Table 1
Autoxidation of polystyrene (PS) to benzoic acid and benzil with selected catalysts

Catalyst (ppm)	Catalyst concentration (mM)	Time (h)	Temperature (°C)	Benzoic acid yield (mol%)	Benzil yield (mol%)
Co/Mn/Br/Zr	6.9/6.9/13.8/0.48	2.0	150	7.1	0.0
Co/Mn/Br/Zr	6.9/6.9/13.8/0.48	2.0	180	26 (4)	0.55 (0.11)
Co/Mn/Br/Zr	6.9/6.9/13.8/0.48	5.0	180	88 (2)	0.60 (0.19)
Co/Mn/Br/Zr	6.9/6.9/13.8/0.48	2.0	220	73	0.10
Co/Mn/Br/Zr	6.9/6.9/13.8/0.48	5.0	220	73	0.0
Co	50	5.0	140	1.0, 2.0	0.04, 0.08
Co/Zr	50/0.5	5.0	140	1.1, 2.4	0.04, 0.07
Co/Mn	50/2.5	5.0	140	12, 38	0.38, 0.66
Co/Ce	50/2.5	5.0	140	14.2	0.61
Co/Ni	50/2.5	5.0	140	1.2	0.04
Ni	50	5.0	140	0.2	0.01
Co/NHPI	3.0/52	5.0	140	3.7	0.16
Co	50	5.0	180	9.1, 5.3	0.21, 0.10
Co/Zr	50/0.5	5.0	180	8.6, 4.2	0.19, 0.06
Co/Mn	50/2.5	5.0	180	56, 49	0.05/0.06
Co/Ce	50/2.5	5.0	180	47	0.28
Co/Ni	50/2.5	5.0	180	8.2	0.15
Ni	50	5.0	180	1.2	0.09
Co/NHPI	3.0/52	5.0	180	11	0.39

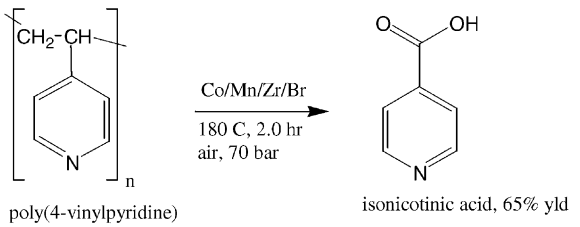
Initial PS concentration = 0.36 M; metal/bromide catalysts with 8% water, the rest in anhydrous acetic acid, NHPI is *N*-hydroxyphthalimide. Parenthesis indicate standard deviation from three independent determinations.

catalyst which has been recently explored [16]. These were much less reactive and gave significantly lower yields. The strong synergistic effect of bromide with transition metals is well documented [8].

The Co/Mn and Co/Ce combinations give higher yields than cobalt itself.

3.3. Autoxidation of poly(4-vinylpyridine)

Isonicotinic acid is the anticipated product from the autoxidation of poly(4-vinylpyridine) because of its structural similarity to polystyrene:



poly(4-vinylpyridine) isonicotinic acid, 65% yld

(8)

The results are given in Table 2. Isonicotinic acid is only partially soluble in acetic acid/water mixtures at room temperature hence a substantial amount of it precipitated upon cooling after reaction. The C,H-NMR spectra of these solids, after washing with water to remove the paramagnetic metals, were identical to authentic isonicotinic acid (4-carboxypyridine). GC analysis indicated the presence of methyl acetate and methanol which are normal by-products of acetic acid decomposition. No isonicotinaldehyde, a common intermediate of 4-methylpyridine autoxidation, was detected via LC. Yields of isonicotinic acid from poly(4-vinylpyridine) of 65% can be compared to those reported from the autoxidation of 4-methylpyridine using a Mn/Br catalyst in

Table 2
Results from the Co/Mn/Zr/Br catalyzed autoxidation of poly(4-vinylpyridine) to isonicotinic acid

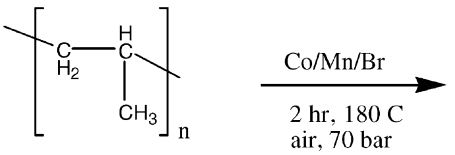
Temperature (°C)	Time (h)	Yield (%; filtrate)	Yield (%; solids)	Yield (mol%; total)
150	2.0	33	0	33
180	2.0	35	30	65
220	2.0	39	24	62
220	5.0	39	21	59

Initial concentration of poly(vinylpyridine) = 0.36 M, Co/Mn/Br/Zr = 6.9/6.9/13.8/0.48 mM, respectively, 8% water in acetic acid.

Table 3
Results from the Co/Mn/Br catalyzed oxidation of 2-poly(vinyl)pyridine-co-styrene to benzoic acid and picolinic acid

Temperature (°C)	Time (h)	[Reagent] (wt.%)	Yield to benzoic acid (mol%)	Yield to picolinic acid (mol%)
150	2.0	3.86	10	0.61
180	2.0	3.84	21	4.3
220	2.0	3.79	81	1.47
220	5.0	3.73	75	0.69

Co/Mn/Br is 7.0/7.0/14 mM, respectively, with 8 wt.% water in acetic acid.



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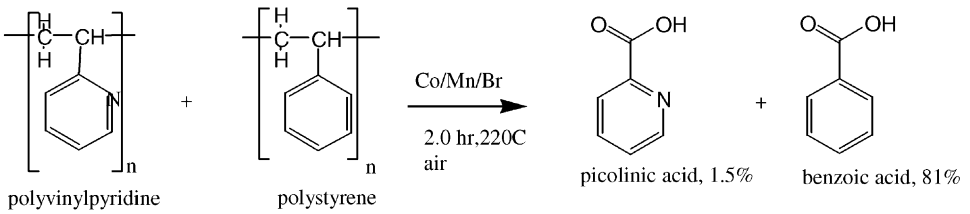
acetic acid (31%) [17], for a HBr catalyst in water (84%) [18], and for a Co/Mn/NHPI catalyst in acetic acid (60%) [19]. It is anticipated that soluble poly(4-vinylpyridine) reacts about an order of magnitude slower than soluble polystyrene since toluene reacts 10 times faster than 4-methylpyridine [8].

3.4. Autoxidation of 2-poly(vinyl)pyridine-co-styrene

The autoxidation of 2-poly(vinyl)pyridine-co-styrene was chosen because it represents a typical copolymer [1] and because 2-methylpyridine has not been successfully oxidized with air. The results are give in Table 3.



(9)

Yields to benzoic acid are comparable to those obtained from polystyrene itself. Previously the autoxidation of 2-methylpyridine acid gave a 3% conversion and 0% yield to nicotinic acid [8]. This is the first time picolinic acid has been reported via homogeneous, liquid phase oxidation howbeit in quite low yield—0.6–4.3 mol%.

3.5. Polypropylene

Autoxidation of isotactic polypropylene in deuteroacetic acid yielded a 53% yield to acetic acid at 180 °C using a Co/Mn/Br catalyst, see Table 4. The yield is based on the moles of acetic acid produced per polymer unit, i.e. it is assumed that during the formation of acetic acid that 1 mol of carbon is lost, presumably to carbon dioxide.

The autoxidation of polypropylene to substantial yields of acetic acid and acetone was also achieved in *water* using vanadium and vanadium/bromide catalysts giving similar yields to those observed in acetic acid. This catalyst/solvent system has been previously reported to aerobically oxidize water insoluble compounds such as methyl- and isopropylaromatic compounds [18]. Slightly higher yields were achieved with V/Br catalysts than with V catalysts and the yields increase somewhat with higher catalyst concentrations, see Table 4. This work contrasts with the previously reported Co catalyzed oxidation of polypropylene in acetic acid which gave very small amounts of acetone and no acetic acid [13]. The thermal, non-catalyzed oxidation of solid polypropylene at 120–170 °C in air gave predominantly acetone while that at 220 and 280 °C gave principally acetaldehyde, the latter in about 3% yield [20].

Twenty-three products are reported during the thermal oxidation of solid polypropylene at 220–280 °C

Table 4
Products from the autoxidation of polypropylene in acetic acid and water solvents

Catalyst	Catalyst concentration (mM)	Solvent	Temperature (°C)	Time (h)	Yield (%)					Others[a] (%)	Others[b] (#)
					HOAc	Acetone	Formic acid	MeOAc or MeOH[c]	HOAc, total		
(1) Co/Mn/Br	6.9	HOAc	150	2	23	1.1 (0.1)	–	5.1 (0.3)	–	–	
(2) Co/Mn/Br	6.9	HOAc	180	2	53	1.1 (0.1)	–	5.6 (0.9)	–	–	
(3) V	4	H_2O	160	4	38	10.2	3.1	0.8	48	28	24
(4) V	4	H_2O	180	4	42	12.6	3.0	0.7	55	16	12
(5) V	4	H_2O	220	2	36	11.8	0.0	0.5	48	12	10
(6) V	4	H_2O	220	4	36	10.3	0.0	0.5	46	10	5
(7) V	85	H_2O	160	4	43	11.0	5.4	1.5	54	27	24
(8) V	85	H_2O	180	4	42	12.1	1.9	1.2	54	16	9
(9) V	85	H_2O	220	2	40	9.9	0.0	0.8	50	9	3
(10) V	85	H_2O	220	4	36	8.4	0.0	0.7	44	10	5
(11) V/Br	4.0	H_2O	160	4	39	11.2	9.0	1.6	50	29	21
(12) V/Br	4.0	H_2O	180	4	39	11.7	6.2	0.8	50	18	14
(13) V/Br	4.0	H_2O	220	2	43	9.7	3.2	2.8	53	12	8
(14) V/Br	4.0	H_2O	220	4	41	2.0	3.1	1.1	43	7	5
(15) V/Br	20.0	H_2O	160	4	42	8.8	10	1.9	51	26	14
(16) V/Br	20.0	H_2O	180	4	35	7.5	7.0	1.7	42	18	3
(17) V/Br	20.0	H_2O	220	2	45	8.3	3.4	2.0	53	10	0
(18) V/Br	20.0	H_2O	220	4	44	8.7	2.8	2.1	53	11	2
(19) V/Br	85	H_2O	160	4	46	11.0	12	2.5	57	20	12
(20) V/Br	85	H_2O	180	4	52	11.0	7.3	2.6	63	11	6
(21) V/Br	85	H_2O	220	2	50	0.6	1.9	1.4	50	6	1
(22) V/Br	85	H_2O	220	4	51	13.2	1.9	3.1	64	13	6

Yields of acetic acid, acetone and methyl acetate were calculated per polymer unit. Formic acid based on carbon present in the polymer. Total acetic acid assumes acetone has been oxidized to acetic acid and includes the acetic acid content of the methyl acetate. Where given parenthesis indicate standard deviation from three independent determinations. Molar concentration of bromide = total moles of metals present. Co/Mn/Br catalyst has 1.0/1.0/2.0 mol ratio, respectively.

[a] GC area of all peaks excluding acetone and acetic acid expressed as percent.

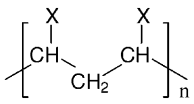
[b] Number of GC peaks excluding acetone and acetic acid.

[c] Methyl acetate in acetic acid and methanol in water.

with acetaldehyde being the main product [20]. Under the vigorous autoxidations described here the intermediate alcohols, ketones, and aldehydes are expected to form the most stable chemical species—acetone and acetic acid. Propylene autoxidation in acetic acid and water also gave many products under mild conditions but these decreased with temperature and with longer times. This can be seen in Table 4 for formic acid, methanol, the number of unknown GC peaks and the total area of the unknown peaks. In examples 3–6 in Table 4, the number of GC peaks decreases monotonically from 24 to 5 as total area of the unknowns decrease from 28 to 10%.

3.6. Mechanism of oxidation of polystyrene, poly(4-vinylpyridine), 2-poly(vinyl)pyridine-co-styrene, and polypropylene

These polymers all have a common structure:where



X = phenyl, 2-pyridine, 4-pyridine, and methyl. Benzoic acid is the expected product from the exhaustive autoxidation of polystyrene (X = phenyl) because compounds of the structure R–Ph (R = ethyl, propyl,

etc.) oxidize to this acid [8]. For X = methyl, acetic acid is the anticipated product because aliphatic hydrocarbons $CH_3(CH_2)_nCH_3$ autoxidize to aliphatic acids $CH_3(CH_2)_{n/2-1}COOH$ [21]. These aliphatic acids then further break down to acetic acid [8,22]. Acetic acid is the most stable aliphatic acid towards autoxidation and is commonly used as an autoxidation solvent [8].

The mechanism of homogeneous liquid phase oxidation metal/bromide catalyzed is a catalyst modified free radical chain mechanism and has been extensively studied [8,9] and their coordination chemistry described [23]. There are many studies of the thermal oxidation of solid polypropylene and polystyrene [20,24–27]. These give insight into some of the initial species formed (peroxy radicals and hydroperoxides on the tertiary C–H bond) and the initial volatile species (for example acetone and acetaldehyde from polypropylene [20]). A *simplified* mechanism to the carboxylic acids, which were primarily observed in this work, is given in Fig. 3. This mechanism does not include a 'backbiting' mechanism which accounts for the higher molecular weight fragments which were observed. This has been described in detail elsewhere [26]. The reaction initiates in Fig. 3 with the formation of a radical species, initially from the adventitious presence of a peroxide [28], and during reaction by (1) a reduced form of bromine indicated by [Br(O)], and (2) another radical $R^\bullet$ in the system. The bromine species are either bromine atoms coordinated to the metal or in the second coordination sphere [23] or dibromine radicals [29]. Bromine atoms are much more selective than $R^\bullet$ radicals with the primary/secondary/tertiary abstraction ratio being 1/200/19,000 for Br and 1/4/47 for $CH_3^\bullet$ [30]. The reaction of the hydrocarbon radical with dioxygen is diffusion controlled to produce the peroxy radical, reaction 12. Reaction 13 is either hydrogen atom abstraction of the peroxy radical with RH or with Co(II) (at Co concentrations >0.01 M):

$$Co(II) + RO_2^\bullet + H^+ \rightarrow Co(III) + ROOH \qquad (11)$$

Reaction 14 is either the thermal dissociation of the weak peroxide bond to generate the unselective hydroxyl radical by the oxidation of Co(II):

$$Co(II) + ROOH \rightarrow Co(III)(OH^-) + RO^\bullet \qquad (12)$$

The alkoxy radical thus produced undergoes β-scission, see reaction 15 which is the chain-splitting event. The carbon atom adjacent to the ketone will be activated and form a secondary radical via hydrogen atom abstraction, reaction 16. A repetition of events leads to the alkoxy radical, reaction 17. This is followed by another β-scission reaction yielding the acyl radical, reaction 18. This subsequently forms the peracid, reaction 19 which then reacts with cobalt(II) to form the acid:

$$XC(=O)OOH + [Co(II)]_2 \rightarrow XC(=O)OH + [Co(III)]_2 \qquad (13)$$

The cobalt(III) generated reactions 13, 14, and 20 is known to react very rapidly with Mn:

$$Co(III) + Mn(II) \rightarrow Co(II) + Mn(III) \qquad (14)$$

This reaction avoids high steady state concentrations of Co(III) which decarboxylate acids readily to

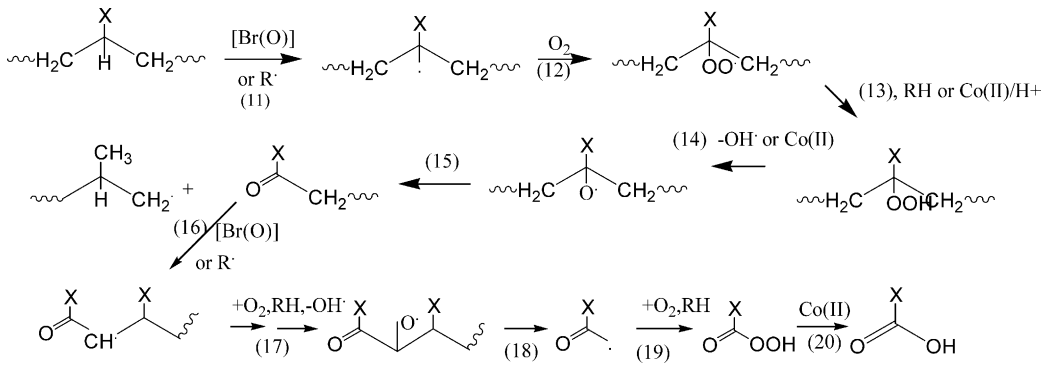


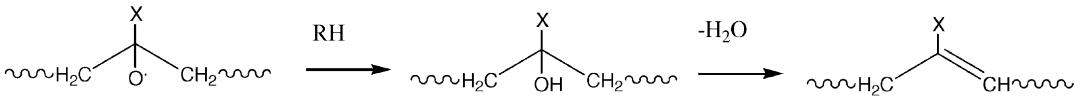
Fig. 3. Mechanism of carboxylic acid formation for polystyrene, poly(4-vinylpyridine), 2-poly(vinyl)pyridine-co-styrene, and polypropylene.

undesirable products. The Mn(III) generates the Br(O) species:

$$Mn(III) + Br^{1-} \rightarrow Mn(II) + [Br(O)] \quad (15)$$

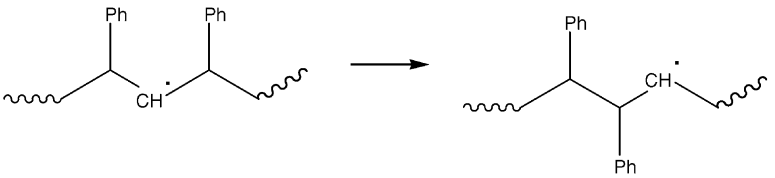
The rapid reactions of cobalt with the peroxides, peroxy radicals, and peracids greatly accelerates the overall reactions and allows for the formation of the carboxylic acids much more rapidly than thermal oxidation.

Olefinic species are known to occur during the autoxidation of alkylbenzenes (for example from ethylbenzene or isopropylbenzene [8]) and is suggested by the GC/MS data (Fig. 1). These can form from the alkoxy radical and subsequent dehydration. The double bond is readily split by metal/bromide catalysts to give carboxylic acids.



(16)

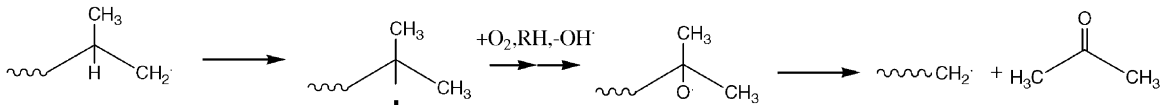
The presence of benzil in the products suggests phenyl migration at some point in the reaction sequence.



(17)

Benzils are known to be cleaved during autoxidation [8].

The acetone formed during the autoxidation of polypropylene could arise from the hydrogen atom transfer as shown below:



(18)

Although hydrogen atom transfers are not common, the driving force here is the formation of the tertiary C–H radical. The subsequent reaction with dioxygen, RH and homolytic cleavage of the hydroperoxide radical leads to the alkoxy radical. The β-scission then yields acetone.

3.7. Autoxidation of polyethylene

The dominant products from the autoxidation of polyethylene are succinic, glutaric, and adipic acid ($HOOC(CH_2)_nCOOH$ where $n = 2$, 3, and 4, respectively). The yields are *defined* as 100× moles acid/((moles of C atoms in polyethylene)/$(2 + n)$) where the moles of C atoms are calculated as weight of polyethylene reacted divided by 14, the latter being the molecular weight of the $–CH_2–$ unit. The $2 + n$ factor recognizes that it takes a linear aliphatic carbon chain of $2 + n$ carbon atoms long to generate the given di-acid. These yields are only approximate due to the presence of short branching chains, see later. The selectivity in Table 5 as defined for succinic acid is 100× succinic acid yield/(total di-acid yield). Polyethylene is virtually insoluble in these solvents but these solutions after reaction, except for those in water, were clear, i.e. no solids were present. In example 14 (Table 5) polyethylene was *initially dissolved* in 80 wt.% dichlorobenzene/20 wt.% acetic acid. The yields were not superior to the other examples in the table although an exact comparison, i.e. identical catalyst concentration and reaction conditions, cannot be made. Table 5 suggests that higher selectivity to succinic acid but at reduced yields can be obtained by increasing the temperature from 150 to 180 (see, examples 1 and 2). A similar trend was observed when using nitrogen oxides and oxygen as the

Table 5
Autoxidation of polyethylene in acetic acid and water solvents

Catalyst	Co or V (mM)[a]	Water (%)[b]	Temperature (°C)[c]	Time (h)	Replicates	Yield (%)[d]	Succinic acid (selectivity, %)	Glutaric (selectivity, %)	Adipic (selectivity, %)
(1) Co/Mn/Zr/Br	6.9	8.0	150	2.0	4	26.6 (6.5)	41.7 (3.1)	35.1 (2.6)	23.3 (3.3)
(2) Co/Mn/Zr/Br	6.9	8.0	180	2.0	3	22.3 (2.4)	62.7 (12)	28.8 (4.8)	8.5 (7.5)
(3) Co/Mn/Zr/Br	13.8	0.0	150	2.0	2	22.1 (1.3)	61.5 (2.8)	30.6 (2.0)	7.9 (0.8)
(4) Co/Mn/Zr/Br	13.8	8.0	150	2.0	3	30.4 (9.7)	39.3 (4.4)	30.6 (6.1)	30.1 (2.6)
(5) Co/Mn/Zr/Br	27.6	0.0	150	2.0	1	32.5	39.7	38.7	21.6
(6) Co/Mn/Zr/Br	27.6	8.0	150	2.0	2	46.3 (1.7)	50.6 (0.2)	17.1 (0.5)	32.4 (0.7)
(7) Co/Mn/Zr/Br	13.8	8.0	150	2.0	3	30.4 (9.7)	39.3 (4.4)	30.6 (6.1)	30.1 (2.6)
(8) Co/Mn/Br	13.8	8.0	150	2.0	1	10.2	0.0	53.1	46.9
(9) Co/Mn/Br	27.6	8.0	150	2.0	1	27.4	40.7	33.0	26.4
(10) Co/Mn/Br	27.6	8.0	150	3.0	1	29.8	43.3	34.2	22.5
(11) Co/Mn/Zr/Br	27.6	8.0	150	3.0	1	32.5	48.0	34.0	18.0
(12) Co/Mn/Zr/Br	27.6	8.0	150	1.0	2	39.0 (1.8)	35.9 (1.6)	27.4 (2.4)	37.6 (0.8)
(13) Co/Mn/Zr/Br	27.6	8.0	150, 180	2, 2	3	32.9 (2.8)	51.6 (5.6)	24.3 (7.3)	24.1 (2.5)
(14, 5) Co/Mn/Zr/Br[e]	10.0	0.0	150, 180	2, 2	3	29.6 (3.0)	42.3 (0.5)	25.6 (1.2)	32.0 (1.4)
(15) V	255	100	180	2.0	1	29.2	24.7	47.9	27.4
(16) V	85.0	100	200	1.0	1	21.5	29.3	33.3	37.4

[a] Molar ratios of Co/Mn/Zr/Br are 1.0/1.0/0.032/2.0.
[b] Percent water in acetic acid.
[c] Examples 13–16 were reactions performed at 150 °C for 2 h followed by 180 °C for 2 h.
[d] Yield is the sum of succinic, glutaric, and adipic acids. Examples 15 and 16 gave acetic acid yields of 13.8 and 11.7%, respectively.
[e] Polyethylene and the catalyst was dissolved in 80 wt.% orthodichlorobenzene/20 wt.% acetic acid.

oxidant [11]. Under the same reaction conditions, addition of 8.0 wt.% water into the acetic acid resulted in higher yields (compare examples 3, 4 and 5, 6). Water normally deactivates autoxidation in acetic acid but apparently it is affecting the yield, in thus far, unknown ways. The addition of Zr to a Co/Mn/Br catalyst results in higher yields (compare examples 6, 9 and 7, 8). Zr, when added in small amounts relative to Co/Mn/Br is known enhance the activity and change the selectivity in autoxidations [8,9]. The yields using a Co/Mn/Zr/Br catalyst are dependent upon the catalyst concentration, see Fig. 4. As the catalyst concentration increases the importance of the selective metal-catalyzed pathways increase as seen, for example, in the autoxidation of 5-hydroxymethylfurfural [9].

The results here can be compared to the use of a NO/O_2 mixture [11]. The autoxidation of low density polyethylene for 16 h at 170 °C gave a yield of 33% di-acids (the latter calculated on the same basis as reported here). Example 6 in table gives a higher yield of 46% at a milder temperature, 150 °C, and significantly less residence time, 2 h. The yields to dicarboxylic acids from solid polyethylene produced from weeks of 280 nm irradiation were approximately 1% [10].

Polyethylene consists of a linear backbone which is periodically interpersed with short chains due to 'backbiting' mechanisms [31]. A detailed NMR analysis, as described in [31] on dissolved polyethylene, is given in Table 6. The initial attack during oxidation will be most favored at the tertiary carbon–hydrogen bond where these short chains join the backbone on the polymer. Table 6 gives 26 branches/1000 $–CH_2–$ groups. This would result in an *average* linear back-

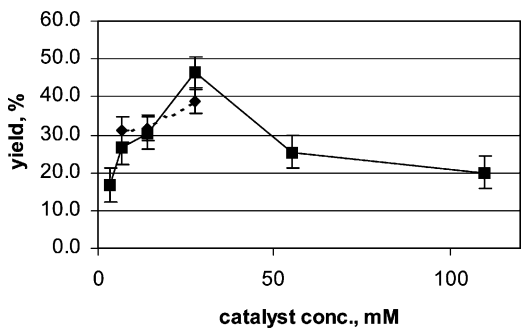


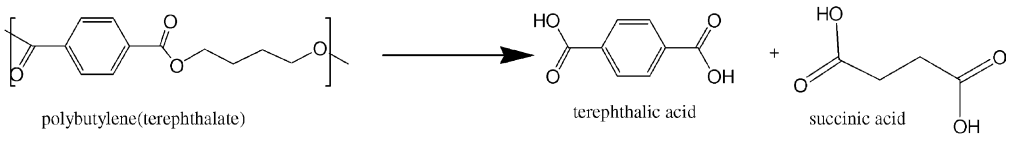
Fig. 4. Yield as a function of catalyst concentration for polyethylene autoxidation. Broken line is Co/Mn/Zr/Br catalyst at 150 °C for 1 h. Solid line is Co/Mn/Zr/Br catalyst at 150 °C for 2 h.

Table 6
Types and amount of branching in the polyethylene

Type of branch[a]	Branches/1000 CH_2
$1B_{4+}$	17.6
$1B_2$	6.2
qB_2	2.8
$3B_5$	2.1
$3B_{6+}$	5.5
$2B_4$	6.7
$2B_{5+}$	7.6

[a] Branches are designated xB_y where y is the length of the branch and x the carbon atom being referred to with the methyl group designated as 1, q is a quaternery carbon atom.

bone chain length, without a branch point, of about 38 carbon atoms, i.e. $–(CH_2)_{38}–$. The presence of the short chains will result in higher yields than calculated in Table 6. This is because, for example, the ethyl and butyl short chains cannot produce succinic and the higher di-acids. Ethyl and butyl short chains are in the highest abundance in polyethylene. Assuming that 50% of the branches were butyl groups, then 5% of the carbon atoms in polyethylene would be unavailable to make the aliphatic di-acids. If each of the short chain



(19)

methyl groups ultimately resulted in acetic acid, then an acetic acid yield of 5.2% would result. Examples 15 and 16 which were performed in water gave acetic acid yields of 13.8 and 11.7%, respectively, suggesting that other mechanisms are operating to produce additional acetic acid.

3.8. Mechanism of polyethylene oxidation

It will be assumed that initially an aliphatic hydrocarbon chain becomes partially exposed (dissolved) to the solvent and catalyst. The thermal autoxidation of long aliphatic hydrocarbons, such as hexadecane, produces alpha–delta (α–δ) and alpha–gamma (α–γ) dihydroperoxides via a 'backbiting' mechanism involving reversible intramolecular hydrogen atom abstraction of the initially formed peroxy radical. These peroxides in turn form α–δ and α–γ hydroperoxyketones [32]. The continued autoxidation of these compounds are expected to produce the observed succinic and glutaric acids, see Fig. 5. A similar mechanism of polyethylene oxidation, dubbed 'zip depolymerization' *starting with a carboxyl radical* has been previously proposed [10].

The mechanism in Fig. 5 shows only one pathway to the di-acids. There certainly are competing pathways starting with the mono-peroxide but these are not shown. The initial radical formation is placed arbitrarily in the beta position relative to the methyl group, reaction 28, Fig. 5. The di-peroxide is formed via a 'backbiting' mechanism, reactions 28–31. The β-scission then occurs and the fragment continues to be oxidized to the di-acids and acetic acid. Reaction 38 is the repetition of reactions 32–37. Considerable yield loss occurs during oxidation of the aliphatic aldehydes as they decarbonylate readily [7].

3.9. Autoxidation of polyesters

The principle products one finds from the aerobic oxidation of poly(butylene)terephthalate (PBT) is terephthalic acid and succinic acid, see Table 7:

Polyesters are formed by esterification of polycarboxylic acids with polyols. Water is one of the products. During preparation of PBT the chain length is increased as increasing amounts of water are removed from esterification reaction. The intermediate chain lengths are referred to as 'oligomers'. During the autoxidation of PBT in 8% water/acetic acid one would expect the process to be reversed:

$$[\mathrm{PBT}]_{\mathrm{solid}} + \mathrm{H_2O} \rightarrow [\text{oligomer}] \rightarrow \text{terephthalic acid} + 1,4\text{-butanediol} \quad (20)$$

$$1,4\text{-butanediol} + \mathrm{O_2} \rightarrow \text{succinic acid} + \mathrm{H_2O} \quad (21)$$

If the hydrolysis reaction to terephthalic acid, reaction 20, was faster than the oxidation reaction, reaction 21, then the succinic acid yields would be as high as that

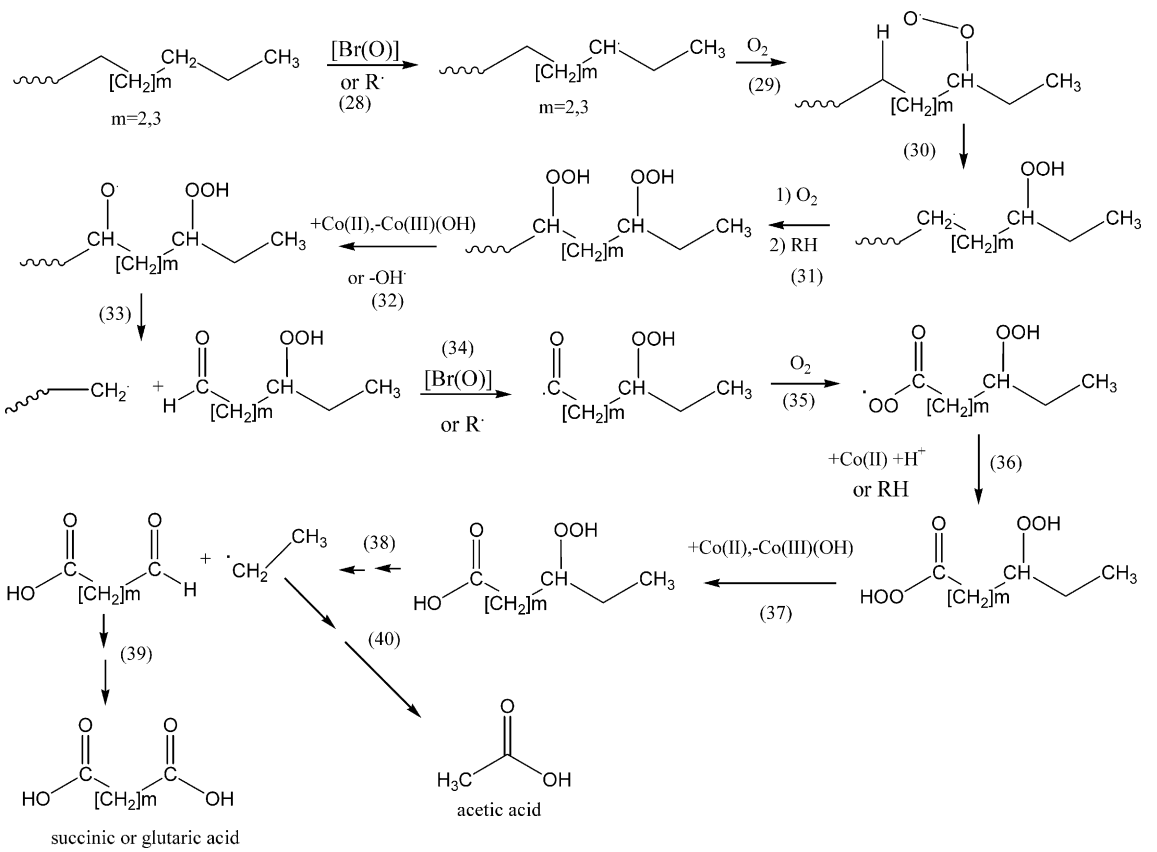


Fig. 5. Mechanism of dicarboxylic acid formation for polyethylene.

obtained starting with 1,4-butanediol itself and quantitative amounts of terephthalic acid would precipitate from solution at room temperature. Terephthalic acid is 99.9% insoluble at room temperature [8]. One find that the succinic acid yields as a function of time do increase, from 2.5–6.0 to 25% as the reaction time is increased from 0.50–1.0 to 2.0 h at 190 °C (examples 1, 6, 8 and 10, 13, 14 in Table 7) *but* the yields are substantially lower than when 1,4-butanediol itself is oxidized (70–82%). This suggests that the oligomer is being directly oxidized at the methylenic carbons of the butanediol producing products other than succinic acid. NMR analysis of the precipitated solids show that both terephthalic acid and oligomer are precipitating at room temperature. One does not know if this oligomer is soluble at the 190 °C reaction temperature. The amount of oligomer in the solids decrease as a function of time as indicated by NMR and elemental analysis, see examples 1, 6, 8 and 10, 13, 14 in Table 7. These observations are also consistent with the oligomer being directly oxidized. Co-oxidations of the PBT with toluene and *p*-xylene were performed since addition of used polyesters during the oxidation of *p*-xylene during normal terephthalic acid manufacture would be a method of recycling. The co-oxidation of toluene with 1,4-butanediol has a lower succinic acid yields (36%) than when 1,4-butanediol is oxidized alone, see examples 2 and 3. Apparently the benzylic peroxy radicals can oxidize the methylenic carbon atoms of 1,4-butanediol. Co-oxidation of PBT with either toluene or *p*-xylene reduces the amount of oligomer in the solids, see examples 1, 4, 5 and 10, 11, 12. The conversion of the toluene and *p*-xylene and the benzoic acid yields is essentially 100% in these experiments. These latter experiments suggest that *p*-xylene can be co-oxidized with PBT which will

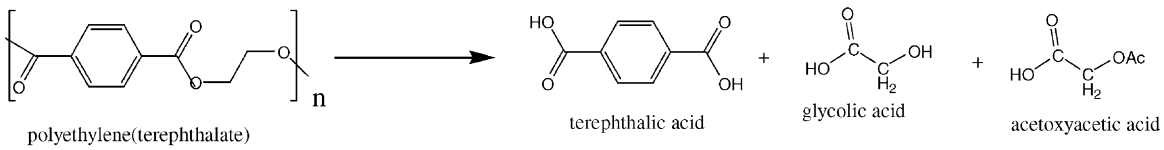
Table 7
Autoxidation of PBT, 1,4-butanediol (BDO), and PBT + Co-oxidants using a Co/Mn/Zr/Br catalyst in 8% water/acetic acid

Example	Source	Initial reagent	Time (h)	C in solids[a] (%)	H in solids[a] (%)	Oligomer in solids (%)	TA yield (%)	Succinic acid
1	1[b]	PBT	0.50	59.29	5.27	40	46	2.5
2	1	BDO	0.50	–	–	–	–	82, 77
3	1	Toluene + BDO	0.50	–	–	–	–	33, 36
4	1	PBT + toluene	0.50	57.57	4.31	22	34	9.7
5	1	PBT + *p*-xylene	0.50	58.06	4.03	5.9	79	7.4
6	1	PBT	1.00	58.17	4.87	–	–	6.0
7	1	PDO	1.00	–	–	–	–	70, 72
8	1	PBT	2.00	57.27	3.5	0.6	56	15, 25
9	1	BDO	2.00	–	–	–	–	70, 75
10	2[c]	PBT	0.50	60.05	4.90	38	53	2.8
11	2	PBT + toluene	0.50	60.27	4.29	20	45	6.7
12	2	PBT + PX	0.50	57.84	3.75	5.9	78	9.9
13	2	PBT	1.00	58.32	4.49	–	–	8.1
14	2	PBT	2.00	57.52	3.77	4.5	47, 49	13, 17

All data at 190 °C using Co/Mn/Br/Zr = 6.9/6.9/13.8/0.48 mM, 0.17 M PBT, 0.21 M, 1,4-butanediol 1.0 M toluene, 0.44 M PX.
[a] PBT contains 65.44% C and 5.50% H; terephthalic acid has 57.83 and 3.65% C.
[b] Source 1 is Crastin® 6134 PBT (E.I. DuPont de Nemours, Wilmington, DE) intrinsic viscosity is 0.75–0.8.
[c] Source 2 is PBT is a crushed bottle resin prepared at DuPont.

lower the amount of precipitated oligomer and higher yields of terephthalic acid, from both the PBT and *p*-xylene, can be obtained.

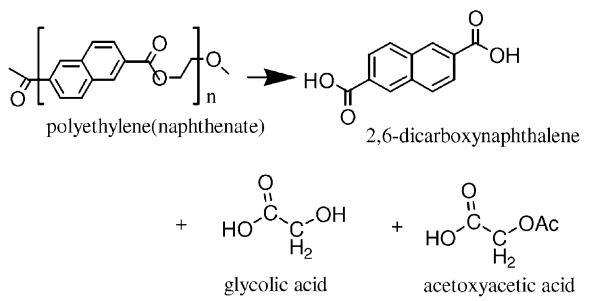
The aerobic oxidation of poly(ethylene)terephthalate yields terephthalic acid, glycolic acid (the partial oxidation product of ethylene glycol) and acetoxyacetic acid (the acetic acid ester of glycolic acid), see Table 8:



(22)

Oxalic acid, which is expected from the oxidation of 1,2-ethanediol, is not seen. Oxalic acid is quantitatively decomposed when oxalic acid itself is heated under the same experimental conditions. Hence the only by-products seen in this reaction are the intermediate glycolic and acetoxyacetic acids. Glycolic acid and acetoxyacetic acid also form from the autoxidation of the acetic acid solvent itself, but the yields are much lower than observed here. Table 8 demonstrates that essentially the same chemistry is occurring with PET as discussed above with PBT.

As expected from the autoxidation of PET, poly(ethylene)naphthenate gives glycolic and acetoxyacetic acid in low yields, see Table 9. 2,6-Dicarboxynaphthalene, similar to terephthalic acid, is 99.9% insoluble at room temperature.



(23)

Table 8
Autoxidation of PET, 1,2-ethanediol, and PET + Co-oxidants using a Co/Mn/Zr/Br catalyst in 8% water/acetic acid

Example	Initial reagent	Time (h)	Oligomer (%)	Terephthalic acid yield (%)	Glycolic yield (mol%)	Acetoxyacetic acid yield (mol%)
1	PET	0.50	37	56	–	–
2	1,2-Ethanediol	0.50	–	–	0.78	5.08
3	1,2-Ethanediol + toluene	0.50	–	–	0.29	3.22
4	PET + toluene	0.50	8	100	–	–
5	PET + *p*-xylene	0.50	10	63	–	–
6	PET	1.00	38	53		
11	PET	2.00	25	56	0.91	6.41
15	PET + *p*-xylene	2.00	0	82	0.21	1.41

All data at 190 °C using Co/Mn/Br/Zr = 6.9/6.9/13.8/0.48 mM, 0.21 M PET, 0.21 M 1,2-ethanediol, 1.0 M toluene, 0.44 M PX.

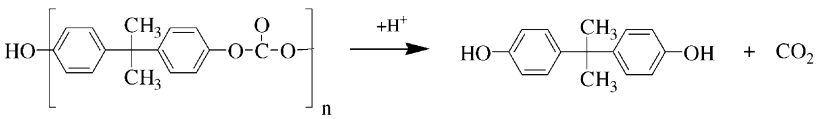
Table 9
Autoxidation of PEN, 1,2-ethanediol, and PEN + Co-oxidants using a Co/Mn/Zr/Br catalyst in 8% water/acetic acid

Example	Initial reagent	Time (h)	NMR analysis of solids	Glycolic yield (mol%)	Acetoxyacetic acid yield (mol%)
1	PEN + toluene	0.50	NDC, BA, oligomer[a]	1.0	2.4
2	PEN	1.0	NDC, oligomer	2.4	4.3
3	PEN + toluene	1.0	NDC, BA, oligomer	1.5	4.1
4	PEN	2.0	NDC, oligomer	1.5	3.7

All data at 190 °C using Co/Mn/Br/Zr = 6.9/6.9/13.8/0.48 mM, 0.16 M PEN, 0.21 M 1,2-ethanediol, 1.0 M, toluene, 0.44 M.
[a] NDC is 2,6-naphthalenedicarboxylic acid and BA is benzoic acid.

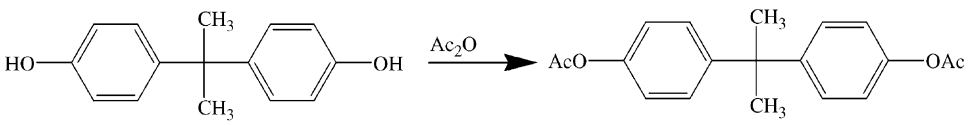
4. Autoxidation of poly(bisphenol A)carbonate (PC)

The aerobic oxidation of poly(bisphenol A)carbonate is an example where we chose a polymer to generate a given high value monomer—4-hydroxybenzoic acid. 4-Hydroxybenzoic acid is a major component in the preparation of liquid crystal polymers [1]. We anticipated that 4-hydroxybenzoic acid could be obtained via (a) hydrolysis, (b) acetylation, and (c) oxidation of polycarbonate. A 21 mol% yield of bisphenol A was obtained when PC was heated for 4 h at 200 °C in 10 wt.% water/acetic acid. This is consistent with the dissolution of PC in acetic acid, a protonic solvent, which would liberate bisphenol A and carbon dioxide:



polycarbonate bisphenol A (24)

Bisphenol is a strong antioxidant whose antioxidant behavior can be masked by addition of acetic anhydride to form the acetate [8,33]:



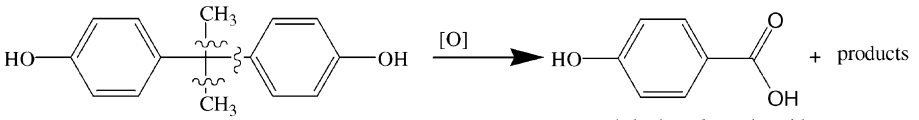
bisphenol A bisphenol A

anhydride to form the acetate [8, 33]: (25)

Table 10
Oxidation of poly(bisphenol A)carbonate (PC) to *p*-hydroxybenzoic acid (PHBA) initial concentration of PC = 0.29 M

Example	Catalyst	Catalyst concentration (mM)	Solvent	Temperature (°C)	Time (h)	PHBA (mol% yield)
1	Co/Mn/Br/Zr	27/27/55/0.88	H_2O/HOAc (10%)	150	5	0.01
2	Co/Mn/Br/Zr	27/27/55/0.88	HOAc	180	5	4.6
3	Co/Mn/Br/Zr	27/27/55/0.88	H_2O/HOAc (10%)	180	5	10.3
4	Co/Mn/Br/Zr	27/27/55/0.88	Ac_2O/HOAc (10%)	180	5	8.2
5	Co/Mn/Br/Zr	110/110/220/0.88	HOAc	220	2	8.0
6	Co/Mn/Br/Zr	27/27/55/0.88	HOAc	220	2	6.9
7	Co/Mn/Br/Zr	27/27/55/0.88	H_2O/HOAc (10%)	220	2	10.1
8	Co/Mn/Br/Zr	27/27/55/0.88	Ac_2O/HOAc (10%)	220	2	5.4
9	Co/Mn/Br/Zr	27/27/55/0.88	H_2O/HOAc (10%)	220	5	9.8
10	Co/Mn/Br/Zr	27/27/55/0.88	Ac_2O/HOAc (10%)	220	5	4.8

Subsequent autoxidation of the bisphenol A diacetate would via cleavage of the *t*-butyl group, yield the 4-acetoxybenzoic acid, reaction 48. The acetate is the normal starting material in the preparation of liquid crystal polymers.



bisphenol A

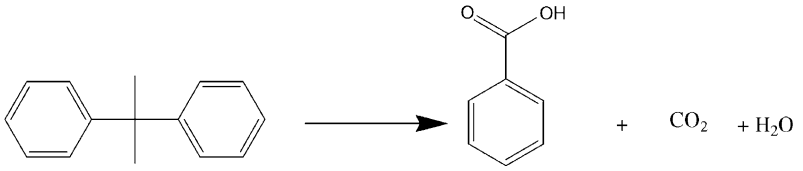
4- hydroxybenzoic acid

(26)

The results are given in Table 10 in which it was attempted to do the hydrolysis, acetylation and autoxidation in a single step. A maximum yield of 4-hydroxybenzoic acid under the conditions utilized is 10%. The formation of 4-hydroxybenzoic acid requires temperatures higher than 150 °C and its yield was enhanced by the presence of water and somewhat by higher catalyst concentrations. The presence of acetic anhydride did not significantly enhance the yield as expected. It may be that the acetylation was slow compared to the oxidation reactions. The higher yields with water initially present may suggest that the hydrolysis of the bisphenol A from the poly(bisphenol A)carbonate may be rate limiting.

The low yields are not only due to the inhibiting effect of the phenols, but the relative chemical inertness of *t*-butyl groups towards autoxidation. *t*-Butyl groups on aromatic rings, and derivatives therefore are subject to attack and cleavage during autoxidation. They do require however significantly more vigorous conditions than methyl- or linear aliphatic aromatic derivatives consistent with their higher C–H bond strength [8]. The GC/MS results are consistent with the breakdown of the *t*-butyl group, see products B, C, D, H, I in Fig. 2. These products will eventually autoxidize to the desired hydroxybenzoic acid.

The Co/Mn/Cl catalyst in combination with a HOAc/chlorobenzene solvent have been claimed to be good conditions to oxidize *t*-butyl groups to carboxylic acids [8,34]. The oxidative cleavage of the model compound 2,2-diphenylpropane was evaluated and compared to the Co/Mn/Zr/Br catalyst in acetic acid, see Table 11.



2,2'-diphenylpropane

benzoic acid

(27)

A yield of 25 mol% was obtained with the Co/Mn/Cl catalyst while only a 5% yield was observed with the Co/Mn/Zr/Br catalyst. This reaction is currently being studied further using the Co/Mn/Cl and also evaluating

Table 11
Results from the oxidation of 2,2-diphenylpropane (DPP)

Catalyst	Catalyst concentration (mM)	Solvent	Time (h)	Temperature (°C)	2,2-DPP, conversion (%)	Benzoic acid yield	Benzoic acid selectivity (%)
Co/Mn/Cl	22/1.4/30	HOAc/Ph–Cl (40%)	4.0	170	2.7	4.9	–
Co/Mn/Cl	22/1.4/30	HOAc/Ph–Cl (40%)	4.0	220	49	26	52
Co/Mn/Br/Zr	55/55/110/0.05	HOAc	1.0	180	0	0	–
Co/Mn/Br/Zr	55/55/110/0.05	HOAc	1.0	220	18	5.3	29

Initial concentration 0.29 M.

the hydrolysis, acetylation and oxidation steps separately.

4.1. Oxidation of poly(vinyl)chloride

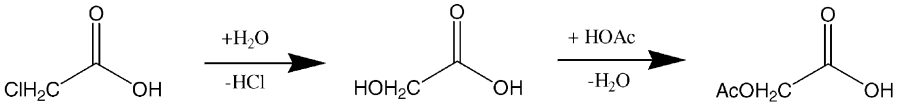
Autoxidation of PVC *in acetic acid* gave monochloroacetic acid in 35% yield with substantial amounts of glycolic acid, and the acetic acid ester of glycolic acid, acetoxyacetic acid, see Table 12. It is not clear what the mechanism for the formation of these products is. Free radical decomposition of PVC has apparently occurred releasing chlorine atoms which then chlorinated the acetic acid solvent. The glycolic acid and acetoxyacetic acid may have originated from the hydrolysis of monochloroacetic acid:

The yields were calculated per polymer unit of PVC added since the stoichiometry of chloroacetic acid from PVC would be written:

$$C_2H_3Cl + O_2 \rightarrow C_2H_3ClO_2 \quad (29)$$

One could obtain high yields of glycolic acid by solvolyzing the monochloroacetic acid to glycolic acid. Assuming this was done, then a 37% yield of glycolic acid could be obtained.

In water, with a V/Br catalyst, succinic acid was observed in 31–38% yield. Co, HBr, Co/Mn/Br catalysts gave much lower yields than V/Br catalyst. The stoichiometry of this reaction, starting with two repeating polymer units of PVC is:



chloroacetic acid glycolic acid acetoxyacetic acid (28)

Table 12
Results for the autoxidation of poly(vinyl)chloride

Example	Catalyst	Catalyst concentration (mM)	Solvent	Time (h)	Temperature (°C)	Chloroacetic acid	Acetoxyacetic acid	Succinic acid	Glycolic acid
1	Co/Mn/Zr/Br	7/7/14/0.25	HOAc	2.0	180	17	0.0	0.0	2.9
2	Co/Mn/Br	13.8/13.8/27.6	HOAc	2.0	180	35	16	0.0	3.3
3	Co/Mn/Br	13.8/13.8/27.6	HOAc	2.0	210	14	0.0	0.0	0.0
4	Co	125	H_2O	2.0	200	–	–	0.0	0.0
5	Co/Mn/Br	20.0/20.0/40.0	H_2O	2.0	200	–	–	1.8	0.0
6	Co/Mn/Br	20.0/20.0/40.0	HOAc/H_2O (50%)	2.0	200	–	–	2.7	0.0
7	HBr	296	H_2O	2.0	200	–	–	1.3	0.0
8	V/Br	85/296	H_2O	2.0	200	–	–	31	0.0
9	Co	125	H_2O	4.0	200	–	–	8.8	0.1
10	Co/Mn/Br	20.0/20.0/40.0	H_2O	4.0	200	–	–	5.9	0.4
11	Co/Mn/Br	20.0/20.0/40.0	HOAc/H_2O (50%)	4.0	200	–	–	7.7	0.9
12	HBr	296	H_2O	4.0	200	–	–	3.0	0.9
13	V/Br	85/296	H_2O	4.0	200	–	–	38	0.0

Initial PVC concentration = 1.22 M (see text for description of yield calculation).

Table 13
Products from the autoxidation of polymers with current production and uses of products (from [35])

Polymer	Product, yield (%)	World production tons per year	Uses of product
PS	Benzoic acid, 88	2.8×10^5 (1994)	Phenol synthesis, preservative, intermediate, others
PVC	Chloroacetic acid, 35	5.7×10^6 (1995)	Carboxymethylcellulose, pesticides, dyes, pharmaceuticals, herbicide
PVC	Glycolic acid via hydrolysis of Cl-HOAc, 38	–	Cleaning agent, chelator, paint solvent
PVC	Succinic acid, 38[a]	–	1,4-Butanediol and tetrahydrofuran synthesis by H_2 reduction
PP	Acetic acid (in H_2O) 63	6.0×10^6 (1994)	Vinyl acetate synthesis, others
PE	Succinic acid, 23	6.2×10^5 (1996)	1,4-Butanediol, tetrahydrofuran
PE	Adipic acid, 15	1.4×10^6 (1993)	Nylon intermediate
PC	*p*-Hydroxybenzoic acid	–	Liquid crystal polymers

[a] Using V/Br in water solvent.

$$C_4H_6Cl_2 + 2O_2 \rightarrow C_4H_6O_4 + Cl_2 \quad (30)$$

The yield was calculated on this basis. Molecular chlorine was not analyzed for. The products observed here are different than the oxalic and benzenecarboxylic acids previously reported when PVC was autoxidized in water at a high pH [14]. No mechanistic hypothesis will be attempted.

4.2. Commercial implications of the autoxidation of used polymers

The products of the autoxidation of the polymers in this study, an estimate of the volume of their world production, and their uses are given in Table 13 [35]. All of the products reported here are current articles of commerce. There are a number of attractive scenarios of this type of recycling done on a commercial scale. For example the product of the polypropylene oxidation in acetic acid would give principally acetic acid as the product—the solvent and the product are the same. Similarly, polystyrene oxidation could be performed in benzoic acid as the solvent [8]. Or if pure, distilled acetic acid was desired, benzoic acid could be the solvent for polypropylene oxidation. The reaction could be operated at above the boiling point of acetic acid hence the acetic acid would flash out of the reactor as it was being made. Or mixtures of polymers could be used. For example mixtures of polystyrene and polypropylene in acetic acid would generate acetic acid and benzoic acid. Benzoic acid is easily separable from acetic acid.

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