[3] a) D. A. Dougherty, *Science* **1996**, *271*, 163–168; b) J. C. Ma, D. A. Dougherty, *Chem. Rev.* **1997**, *97*, 1303–1324.

[4] a) J. Benkhoff, R. Boese, F.-G. Klärner, *Liebigs Ann./Recuil* **1997**, 501–516; b) F.-G. Klärner, J. Benkhoff, R. Boese, U. Burkert, M. Kamieth, U. Naatz, *Angew. Chem.* **1996**, *108*, 1195–1198; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1130–1133; c) F.-G. Klärner, U. Burkert, M. Kamieth, R. Boese, J. Benet-Buchholz, unpublished results.

[5] All methods of calculation used here are implemented in the program package SPARTAN 4.0, Wavefunction Inc., 18401 Von Karman, Suite 370, Irvine, CA 92715 (USA).

[6] For the use of semiempirically calculated EPSs for the qualitative prediction of the bond strength between aromatic molecules and cations, see also a) S. Mecozzi, A. P. West, D. A. Dougherty, *Proc. Natl. Acad. Sci. USA* **1996**, *93*, 10566–10571; b) S. Mecozzi, A. P. West, D. A. Dougherty, *J. Am. Chem. Soc.* **1996**, *118*, 2307–2308.

[7] The qualitative assessment of the EPSs for the prediction of bonding properties has also been successfully applied for other guest molecules not discussed here: F.-G. Klärner, U. Burkert, M. Kamieth, A. E. Wigger, unpublished results.

[8] a) C. Seel, F. Vögtle, *Angew. Chem.* **1992**, *104*, 542–563; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 528–549; b) T. Z. Mondasini-Denti, W. F. VanGunsteren, F. Diederich, *J. Am. Chem. Soc.* **1996**, *118*, 6044–6051.

[9] a) D. A. Stauffer, R. E. Barrans, D. A. Dougherty, *Angew. Chem.* **1990**, *102*, 953–956; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 915–918; b) A. McCurdy, L. Jimenez, D. A. Stauffer, D. A. Dougherty, *J. Am. Chem. Soc.* **1992**, *114*, 10314–10321; c) S. M. Ngola, D. A. Dougherty, *J. Org. Chem.* **1996**, *61*, 4355–4360.

[10] This is of course strictly true only for the gas phase, as different solvation of the receptor molecules could undoubtedly compensate for this effect.

[11] a) L. E. Chirlian, M. M. Francl, *J. Comput. Chem.* **1987**, *8*, 894–905; b) C. M. Breneman, K. B. Wiberg, *J. Comput. Chem.* **1990**, *11*, 361–373.

[12] a) R. C. Haddon, *Science* **1993**, *261*, 1545–1550; b) R. C. Haddon, *Acc. Chem. Res.* **1988**, *21*, 243–249; c) P. W. Rabideau, A. Sygula, *Acc. Chem. Res.* **1996**, *29*, 235–242.

[13] D. Philp, J. F. Stoddart, *Angew. Chem.* **1996**, *108*, 1242–1286; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1154–1196.

[14] P. L. Anelli, P. R. Ashton, R. Ballardini, T. T. Goodnow, A. E. Kaifer, D. Philip, M. Pietraszkiewicz, L. Prodi, M. V. Reddington, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, C. Vincent, D. J. Williams, *J. Am. Chem. Soc.* **1992**, *114*, 193–218.

[15] G. R. Desiraju, *Angew. Chem.* **1995**, *107*, 2541–2558; *Angew. Chem. Int. Ed. Engl.* **1995**, *32*, 2328–2345.

Chemical Recycling of Plastics to Useful Organic Compounds by Oxidative Degradation**

Anne Pifer and Ayusman Sen*

With the production of polymeric materials on the rise and landfill space at a premium, it becomes increasingly important to develop new techniques for reducing the amount of material lost to the landfill. Approximately 20% of landfill volume in the USA is consumed by plastics, and their lack of compatibility with the environment has generated much interest in increasing the amount of polymeric material that is reclaimed as structural material or chemically degraded to fuel or useful organic compounds.[1]

Chemical recycling, which has been increasingly applied in recent years, is defined as the breakdown of polymeric waste into materials that are reusable as fuel or chemicals, including monomers.[1a,c,d, 2] Most chemical recycling being done today focuses on the use of refinery technology and equipment to convert polymers into hydrocarbon feedstocks. Additionally, the depolymerization of condensation polymers, such as poly(ethylene terephthalate), to reusable monomeric material is currently practiced.[3] Of the 27 million tons of plastic material produced in the USA each year, 25% is condensation polymers, while addition polymers constitute 75% of this weight.[4] Addition polymers may be chemically recycled in refineries; however, the price of crude oil and hydrocarbon mixtures produced must compete with oil prices to be economically viable, and the risk to refinery equipment is high when postconsumer mixed plastics are used.[5, 2] Dufaud and Basset have reported a mild new procedure for the catalytic hydrogenolysis of polyolefins.[6] Here we describe a new oxidative degradation procedure that converts the most widely used (addition) polymers—such as polystyrene, polyethylene, and polypropylene—into useful organic compounds, including monomers for other polymerizations. The recycling of these polymers is currently problematical owing to the high costs of collection and sorting, the small difference in prices for virgin and recycled resins, and the reduction in polymer properties caused by the incompatibility of different plastics components.[7] These economic barriers could be overcome if the products generated from these polymers were more valuable and if mixed plastics could be processed together, eliminating sorting costs.

The oxidative degradation of the polymers involved reaction with nitrogen oxides and dioxygen at 170 °C. The results obtained are summarized in Table 1.

Polystyrene with average relative molecular weight of 280000 was converted into a mixture of benzoic acid, 4- and 3-nitrobenzoic acids, and gaseous oxides of carbon under the standard reaction conditions (170 °C, 16 h; partial pressures: 275 kPa NO, 690 kPa O_2, 3170 kPa N_2). No unchanged polymer was detected by ^{1}H NMR spectroscopy. The ratio of benzoic acid to nitrobenzoic acids varied significantly with NO and O_2 content in the reaction mixture; no reaction occurred without the presence of both gases. At a high partial pressure of NO (690 kPa), no benzoic acid was formed, 4-nitrobenzoic acid was the major product, and other nitro species were detected in trace amounts. On the other hand, at a low partial pressure of NO (175 kPa), benzoic acid and unchanged polystyrene predominated, and only trace amounts of nitrobenzoic acids were detected. In reactions where the partial pressure of NO was reduced (140 kPa) and that of O_2 increased (1035 kPa), all the polymer was converted, and the molar ratios of benzoic acid, 4-nitrobenzoic acid, and 3-nitrobenzoic acids were 7:1:1. In general, a O_2 partial pressure of 690 kPa or more was necessary for the reaction to proceed to completion. Benzoic acid, 4-nitrobenzoic acid, and 3-nitrobenzoic acid are easily separated by

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Table 1. Oxidative degradation of polymers by the NO_x/O_2 system.[a]

Polymer	Amount of starting material [g]	Amount of nonvolatile products [g]	Products	amount [g]
polystyrene ($M_\mathrm{w} = 280000$)	0.26	0.19	benzoic acid	0.08
			4-nitrobenzoic acid	0.02
			3-nitrobenzoic acid	0.02
			3,5-dinitrobenzoic acid	traces
high-density polyethylene[b]	0.27	0.21	succinic acid	0.08
			glutaric acid	0.07
			adipic acid	0.02
			pimelic acid	0.03
			unknown organic compounds	traces
low-density polyethylene[b]	0.26	0.22	succinic acid	0.08
			glutaric acid	0.06
			adipic acid	0.02
			pimelic acid	0.01
			unknown organic compounds	traces
polypropylene[c] ($M_\mathrm{w} = 250000$)	0.26	0.15	acetic acid	
			unknown organic compounds	
polymethyl methacrylate ($M_\mathrm{w} = 96200$)	0.26	0.15	oligomers ($M_\mathrm{w} = 985$)	
polyacrylic acid[d] ($M_\mathrm{w} = 450000$)	0.25	0.10	oligomers	
nylon-6,6[e]	0.26	0.16	succinic acid	0.01
			glutaric acid	0.01
			adipic acid	0.06
			acetic acid	traces

[a] Standard conditions: 275 kPa NO, 690 kPa O_2, 3170 kPa N_2; 170°C; 16 h. [b] Reaction with 1035 kPa O_2. [c] Reaction with 480 kPa NO. [d] Reaction at 135 °C

sublimation. While lab-grade polystyrene was employed in most experiments, similar results were also obtained starting with styrofoam cups and polystyrene packing material (Figure 1).

Figure 1. Polystyrene packing material before (left) and after reaction (right) under the standard conditions (170 °C, 16 h; partial pressures: 275 kPa NO, 690 kPa O_2, 3170 kPa N_2). Part of the product mixture can be seen as a sublimate on the liner walls. No unchanged polymer remained.

It appears that the nitrobenzoic acids and benzoic acid arise from polystyrene through two independent parallel pathways. The former are generated by attack on the aromatic ring prior to cleavage of the polymer backbone. On the other hand, benzoic acid is generated by oxidation of the polymer backbone. After benzoic acid is formed, the carboxylic acid substituent deactivates the ring towards nitration. This mechanistic scenario is supported by the observation that under the same reaction conditions isopropyl benzene cleanly yielded benzoic acid.

When the standard reaction conditions were employed, both high-density polyethylene pellets ($d = 0.962$) and low-density polyethylene powder ($d = 0.915$) produced mixtures of short-chain α,ω-diacids (pimelic acid, adipic acid, glutaric acid, and succinic acid) in good yields (73 and 65%, respectively, by weight relative to the starting material) along with oxides of carbon. Only trace amounts of malonic acid were detected owing to its decomposition at temperatures above 135 °C. No unchanged polymer was detected by ^1H NMR spectroscopy, and mass spectrometry indicated that oligomers with molecular weights of less than 350 were present in trace quantities. The formation of α,ω-diacids is noteworthy since these can be used as monomers in condensation polymerizations to yield commercially important polyamides and polyesters.[8]

When adipic acid was subjected to the standard reaction conditions, the product mixture consisted of unchanged adipic acid along with glutaric acid and succinic acid. This is consistent with a mechanism involving loss of carbon dioxide from a carboxyl radical followed by further oxidation of the resultant alkyl radical to the lower carboxylic acid. However, the good yield of α,ω-diacids precludes the possibility of products forming predominantly by successive decarboxylations starting with a long-chain carboxylic acid. Instead, the majority of the α,ω-diacids must arise through zip depolymerization via a series of cyclic transition states resulting from an attack of the carboxyl radical on the chain (backbiting mechanism). Such a series of steps has been postulated in the photooxidation of low-density polyethylene, although the latter reaction leads to a far more complex mixture of products.[9]

The reaction of isotactic polypropylene ($M_\mathrm{w} = 250000$) under standard conditions resulted in a complex mixture of oligomeric and polymeric materials, as well as low molecular weight organic compounds. Upon increasing the partial pressure of NO to 480 kPa, the product mixture simplified to organic compounds with molecular weights below 155, as observed by mass spectrometry. No polymer remained, and the organic compounds were completely soluble in acetone (unlike the starting material or the products observed when 275 kPa NO was employed). The organic molecules formed consisted of ketones and carboxylic acids, including acetic acid. As with polyethylene, a backbiting radical mechanism is a possibility, as has been observed for the photooxidation of polypropylene.[10]

Nylon-6,6 was subjected to the standard reaction conditions (except at 135 °C), and a mixture of α,ω-diacids was produced: adipic acid, glutaric acid, and succinic acid. When the reaction was conducted at 110 °C, acetic acid, formic acid, and ammonium ion were observed in trace quantities along with an insoluble black solid. These products were evidently formed by the oxidation of the diamine portion of the nylon-6,6 backbone since similar products were observed from the oxidation of hexamethylenediamine under the standard conditions.

Both polymethyl methacrylate and polyacrylic acid were oxidized under standard conditions to give oligomeric materials with drastically reduced molecular weights. For example, polymethyl methacrylate with $M_w = 96200$ and a polydispersity of 1.5 was oxidized to products with $M_w = 985$ and a polydispersity of 1.7, as observed by gel permeation chromatography in chloroform.

In conclusion, a wide variety of addition and condensation polymers can be oxidatively degraded under relatively mild conditions by a mixture of nitrogen oxides and dioxygen. In the particular cases of polystyrene, high- and low-density polyethylene, and perhaps polypropylene useful organic compounds are produced in moderate to good yields. The procedure is less useful for condensation polymers, such as nylon-6,6, since these can in principle be hydrolyzed back to the starting monomers.

Experimental Section

The reactions were carried out in 125-mL Parr pressure reactors with glass liners. Typically, the polymeric material (approx. 0.25 g) was added to a glass liner and then placed into the reactor, which was sealed. The reactor was purged with N_2, and then pressurized to 275 kPa with NO, to 3445 kPa with N_2, and finally to 4135 kPa with O_2. The reactor was heated to 170 °C for 16 h, following which it was cooled and the pressure released. The product mixture was then removed and analyzed by one or more of the following techniques: NMR spectroscopy, mass spectrometry, and gel permeation chromatography.

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[1] Reviews: a) C. P. Rader, S. D. Baldwin, D. D. Cornell, G. D. Sadler, R. F. Stockel, *Plastics, Rubber, and Paper Recycling*, American Chemical Society, Washington, **1995**; b) G. D. Andrews, P. M. Subramanian, *Emerging Technologies in Plastics Recycling*, American Chemical Society, Washington, **1992**; c) F. P. La Mantia, *Recycling of Plastic Materials*, ChemTec, Toronto-Scarborough, **1993**; d) R. D. Leaversuch, *Mod. Plast.* **1991**, *68*, 40–43; e) R. S. Stein, *Proc. Natl. Acad. Sci. USA* **1992**, *89*, 835–838.

[2] W. Kaminskiy, *J. Phys. IV* **1993**, *3*, 1543–1552.

[3] a) W. De Winter in ref. [1c], pp. 1–15; b) ref. [1d].

[4] G. Mackey in ref. [1a], pp. 161–169.

[5] M. W. Meszaros in ref. [1a], pp. 170–182.

[6] V. Dufaud, J.-M. Basset, *Angew. Chem.* **1998**, *110*, 848–852; *Angew. Chem. Int. Ed.* **1998**, *37*, 806–810.

[7] C. P. Rader, R. F. Stockel in ref. [1a], pp. 2–10.

[8] Review: H. R. Kricheldorf, *Handbook of Polymer Synthesis, Part A*, Marcel Dekker, New York, **1992**, chap. 11, 14.

[9] S. Karlsson, M. Hakkarainen, A.-C. Albertsson, *Macromolecules* **1997**, *30*, 7721–7728.

[10] S. Girois, L. Audouin, P. Delprat, J. Verdu, *Polym. Degrad. Stab.* **1996**, *51*, 133–141.

Investigation of the Molecular Recognition of Amino Acids by Cyclopeptides with Reflectometric Interference Spectroscopy[**]

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Molecular recognition plays a crucial part in many biological processes where guest molecules are bound very selectively and reversibly by their host. These mostly enantioselective recognition processes, in which chiral ligands interact with their receptors, can be imitated with synthetic molecules.[1] Synthetic receptors have various possible applications in the medical and pharmaceutical field, as new separation-phase material or sensitive coatings.[2] In fundamental research, important insights into the type of interaction in host–guest complexes are gained.[3] A multitude of different macrocyclic receptors such as crown ethers, cyclophanes, cyclodextrins, calixarenes, and cyclopeptides has already been synthesized.[4] With the cyclopeptides cyclo(Pro-Gly)$_3$ and cyclo(Pro-Gly)$_4$ the distinction between D and L amino acid salts in $CDCl_3$ became possible with NMR spectroscopic methods.[5] With macrocyclic peptides, chiral amines were distinguished,[6] and zwitterionic amino acids were complexed with chiral crown ethers.[7] These examinations of interactions between cyclopeptides and analyte were carried out with complicated methods.

We now report on novel sensor modules with surface-bound cyclopeptides as molecular receptors. In earlier work we were able to prove that cyclohexapeptide libraries can be used as chiral selectors in capillary electrophoresis.[8] With combinatorial solid-phase synthesis a host of such detector molecules can be produced.[9] Compared with singular procedures, as for calixarenes and cyclodextrins, our strategy shows a higher diversity by several orders of magnitude (virtual library: 10^{16} cyclohexapeptides from commercially available starting materials) and therefore a better chance of finding a receptor lead structure. Cyclohexapeptides are limited in their conformation,[10] and many basketlike structures can be synthesized by modifying the side chains. Based on these findings we immobilized the cyclopeptides **1**–**3** (Figure 1) on glass surfaces that function as transducers. The interaction between the cyclopeptide and the analyte is examined with reflectometric interference spectroscopy (RIfS).[11] In this optical method of detection, the reflection and the interference of light at phase boundaries are used for the time-resolved determination of changes in the optical film thickness (product of refractive index n and physical film thickness d) of thin transparent films from the resulting interference

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