New Pathways in Plastics Recycling

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Plastics waste is today recovered, reprocessed, or used as raw material or fuel in a number of processes. Current legislation in Germany has acted as a driving force for the recycling of plastic waste. The book *Recycling and Recovery of Plastics* by Brandrup[1] provides a review of the various methods and processes. Mechanical treatment to recyclates or incineration with energy utilization lie at the forefront of economic interest. Except for energy utilization no satisfactory solutions have yet been found for contaminated or mixed plastics or, in particular, composite plastics since articles made from such old plastic materials usually exhibit unsuitable mechanical properties. On the other hand, in view of the large and still strongly growing quantities of plastic produced, plastic waste represents a significant source of raw materials, one which until now has been inadequately exploited for the production of valuable chemical products. This form of raw material utilization could offer economic advantages and reflect recycling philosophy, for in this way the material cycle is closed.

Polyolefins in particular, which in quantity terms represent the largest group of plastics, are frequently used as packaging material and rapidly reappear as waste. Because they consist only of carbon and hydrogen atoms they are also called "solid oil".

Consequently many research groups in universities and industry have in the past investigated not only direct recycling but also the use of plastics as raw materials when the polymer molecules are degraded into small, organic base materials which can be purified by distillation or other methods.

However, because of chemical and technical problems as well as economic and legal factors, all processes for recycling of mass-produced plastics as raw materials have not been cost effective until now. Catalytic degradative reactions, such as those recently published by Dufaud and Basset,[2] Uemichi et al.,[3] and Pifer and Sen[4] have now provided a new stimulus.

Particularly spectacular is the selective degradation of polyethylene with zirconium hydride catalysts at only 150 °C upon addition of hydrogen, as described by Dufaud and Basset.[2] Reversal of the polymerization by Ziegler catalysts occurs, leading to short-chain hydrocarbons. This result is

illustrative of the effort devoted to recovery of the corresponding monomers from the plastic waste where possible.

Unfortunately the monomers cannot easily be recovered quantitatively from mass-produced plastics, including polyethylene (PE) and polypropylene (PP). In contrast, monomer recovery from specialty plastics such as polymethylmethacrylate (PMMA), polystyrene (PS), and polytetrafluorethylene (PTFE) has already been carried out successfully in high yields. In certain cases this method has been used technically when valuable monomers increased the profitability. Chemical research is therefore directed at recovering the respective monomer in high yield and purity.

The Current Status of Plastics Recycling as a Source of Raw Materials

Because of the low cost effectiveness of recycling plastics for raw materials there have been few technical applications until now. Therefore plastic waste is still mainly
- dumped (total loss of materials and energy);
- materially recycled, usually to products of lesser value (loss of quality), particularly if plastic mixtures are used;
- thermally recycled in municipal waste incineration plants or steel works (material loss).

In the case of bulk plastics the methods currently developed for recycling as raw materials have found few industrial applications. Nevertheless scientific interest in this topic remains undaunted. The reasons are clear:
- Considerable economic interest in the complete degradation of plastics and the recovery of high-value products exists because of high dumping costs and legal requirements for recycling.
- The unsolved chemical problems present a challenge to modern scientists. Particular aspects are the inertness of the polyolefins and the thermodynamic limitations to polymer reversal.

Separation and purification of plastic mixtures will be critical for recycling as raw materials. In a few cases monomer recovery has been remarkably successful with specialty plastics and has been used technically on a larger scale. Thus, up to 97 % of monomer was recovered from PMMA in a fluidized bed process at 450 °C.[5] A conversion of the plants that currently run the depolymerization in lead baths over to this process is planned. Polystyrene may also be extensively depolymerized to monomers at 550 °C; in addition to 77 % styrene, 13 % oligomers are also formed. The purity achieved

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at present is still too low, however, to allow economic operation.

The pyrolysis of PTFE is remarkable. In the past only 16% of the monomer could be recovered. Recently by optimization of a fluidized bed process and at a cleavage temperature of 605 °C 78% tetrafluoroethene, 5% hexafluoropropene, and 4% perfluorocyclobutane were obtained.[6] Fluidization with water vapor was critical for the high yields of these usable fluoroolefins.

In addition to thermal cleavage, solvolysis (alcoholysis) of the important polyester polyethylene terephthalate (PET) to terephthalic acid derivatives and glycol has been used technically.[1]

The technical implementation of chemical recycling relies fundamentally on well-proven process concepts. Pyrolysis is carried out either as a melt continuous in stirred tank reactors, in a fluidized bed, or in a rotary kiln, while solvolysis is normally undertaken in a stirred vessel under pressure. A problem with all processes is the contamination of used plastic and the uniformity of type of the materials used. In this context high proportions of PVC still cause difficulty because of the formation of HCl and corrosion, although there has been no lack of attempts at dehalogenation. Composites, particularly those with metals, can impair reutilization. Used, mixed, and contaminated plastics must therefore normally be mechanically treated and, to a lesser extent, also thermally pretreated.

One interesting possibility for the separation of plastics mixtures could be the staged pyrolysis investigated by Bockhorn: Different components are depolymerized or destroyed one after the other with a temperature program.[7] The development potential of this method has yet to be established.

Catalysts in Recycling Polyolefins for Raw Materials

Polyolefins prepared from olefins such as PE and PP are kinetically relatively inert and more closely resemble paraffins in their chemical behavior. Until now there has been no way to degrade these polyolefins selectively at low temperatures to give homogeneous hydrocarbon products (especially olefins).

In contrast thermal cleavage (pyrolysis) is a well-established method for the degradatin of polyolefins. Under severe reaction conditions (> 450 °C) cleavage of the polymer chain occurs as the primary reaction with sufficient speed—considerable amounts of heat must be mustered to cleave the C−C bond. The radical fragments formed undergo complicated and less selective secondary reactions that are difficult to control under the conditions of the primary reaction and are in effect analogous to the reactions of crude oil cracking. The product spectrum of pyrolysis is determined primarily by these secondary reactions, so that special efforts have been made to direct the reaction thorugh the use of catalysts.

As always, the action of the catalyst is based on the formation of reactive intermediates to reduce the activation energy of the corresponding partial reaction and thus increase the rate of reaction. The enthalpy of bond cleavage cannot be influenced by the catalysts. In the degradation of polyolefins it

is reasonable to use the same or similar catalysts that were used in their preparation. From a mechanistic viewpoint reversal of the Ziegler–Natta polymerization is, according to the principle of microreversibility, theoretically possible. However, for thermodynamic reasons this reaction is limited because selective transfer of the relatively high depolymerization enthalpy to the reactants is difficult.

In this context Dufaud and Basset have succeeded in activating the C−C bond in PE catalytically with a strongly electrophilic Ziegler–Natta catalyst and cleaving it by the action of hydrogen at 150 °C.[2] A zirconium monohydride— obtained by condensation of tetraneopentylzirconium with the silanol groups on the surface of a partially dehydroxylated alumosilica gel and subsequent hydrogenation with H_2—was used as catalyst. Dufaud and Basset suggest two structures which are characterized by the close spatial relationship of the zirconium hydride to the silicon dihydride or aluminum hydride (Figure 1). This compound is able to polymerize
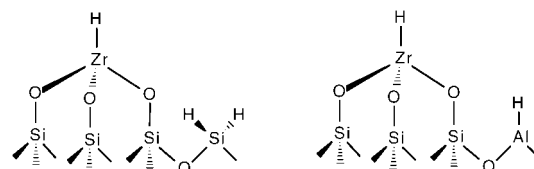

Figure 1. Suggested structures for zirconium hydride on alumosilica gel (according to Dufaud and Basset).[2]

ethene as well as propene. The polymer thus formed and bound to the catalyst could be cleaved hydrogenolytically to lower alkanes under a hydrogen atmosphere at 150 °C. After 15 h the polymer was completely degraded to ethane and methane. Not only polymer generated in situ, but also normal commercial polyethylene was degraded in the same way. Initially oligomers were formed which were then further cleaved to lower alkanes.

The mechanism proposed by Dufaud and Basset is based on endothermic β-alkyl transfer and subsequent exothermic hydrogenation (Figure 2). It is clear that this degradation reaction is not a "true" depolymerization (i.e., retro-polymerization) where starting from an active end only monomers are cleaved. Formally regarded this is a statistical chain cleavage which, because of the involvement of hydrogen, may even be considered to be a retro-polycondensation. Nevertheless, this discovery is remarkable since for the first time a catalyst has been found that is actively involved in the primary reaction. Even if in this case no monomers were obtained, catalytic monomer recovery is a large step closer. The specific production of olefins with suitable input of cleavage energy is the main problem for the realization of retro-polymerization.

Another possibility for the application of catalysts is to use cracking or superacid catalysts that are well-known for crude-oil processing, and to test their suitability for plastic pyrolysis.[8] For example, zeolite catalysts which frequently exhibit active metal centers may be used. It is no wonder, therefore, that more recent work on plastics degradation has been concerned with similar systems. Uemichi et al. have inves-
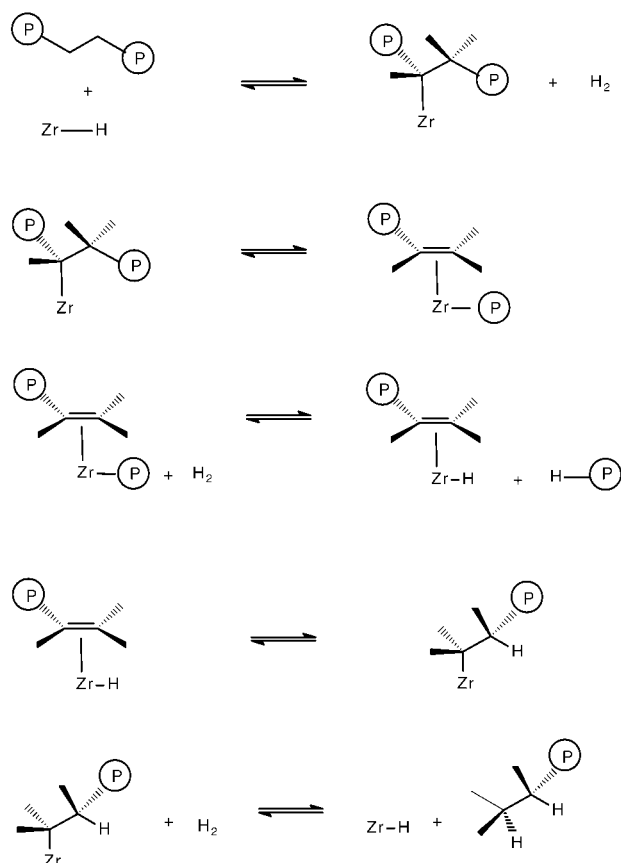
Figure 2. Mechanism of the hydrogenolysis of polyethylene (according to Dufaud and Basset).[2] Ⓟ = polymer chain.

tigated the catalytic degradation of low-density polyethylene (LDPE) with different catalysts.[3] Here, a PE melt was passed slowly into a fixed-bed reactor heated to 525 °C through which helium is passed. The resulting products were captured and analyzed. In contrast to the non-catalyzed reaction, aromatic oils were formed in large amounts depending upon the catalyst, but rarely olefins. The high pyrolysis temperature of 400 – 525 °C showed clearly that secondary reactions are effectively catalyzed by this route, the primary reaction, however, proceeds largely unaltered.

Ibrahim and Seehra have investigated by ESR spectroscopy the cleavage of PE/PP mixtures in the presence of sulfur the zeolite HZSM-5, and nickel/molybdenum on Al_2O_3.[9] In this way they determined the number of radicals formed in relation to temperature and catalyst. They found that upon addition of sulfur or sulfur with NiMo/Al_2O_3 radicals were formed at temperatures as low as 280 and 240 °C, respectively. In contrast, with pure PE/PP or upon addition of HZSM-5 the radicals could only be observed at 360 °C. The number of radicals formed upon addition of sulfur was several times higher than without catalyst addition, but significantly lower when other catalysts were used. The precise nature of the effect of sulfur addition is still unclear. The action of HZSM-5 and NiMo/Al_2O_3 is attributed to the hydrogenation of the free radicals.

Unusual methods which initiate the partial oxidative decomposition of plastics by the action of nitrogen oxides and oxygen should not go unmentioned. Pifer and Sen were able to show, for example, that at 170 °C small amounts of valuable organic acids could be obtained from a number of different polyolefins.[4] This cannot be an example of catalysis because NO_x and O_2 do not emerge from the reaction unscathed. Instead, it is better to use the term initiation. However, the principle is interesting because the carbon chain is cleaved at low temperatures.

Even though the promising developments for polyolefins and plastic mixtures described here still have to find industrial application, they do show a way by which raw materials obtained by recycling lead to more valuable products and hence to an improvement in the cost efficiency of the processes.

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