Poly(vinyl chloride) on the Way from the 19th Century to the 21st Century*

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ABSTRACT: Despite all the technical and economic problems and the public discussions on the environmental dangers and hazards of chlorine chemistry, poly(vinyl chloride) (PVC) is the second most produced plastic (with a worldwide capacity of about 31 million tons), placing after polyolefins and before styrene polymers. Presently, PVC production worldwide is growing at a rate of more than 4% per year. The application of PVC was first described in a patent in 1913, but only after 1930 did a sustained interest in PVC arise in several industrial laboratories. The most remarkable milestones in PVC history and their importance to the development of macromolecular chemistry are briefly described, and some present PVC research and industrial applications, with respect to polymerization, stabilization, bulk property modification, and chemical and material recycling of PVC waste, are discussed. Some actual selected topics include the emulsion polymerization of vinyl chloride with polymeric surfactants and controlled free-radical polymerization with nitroxyls, whereas ionic and metal organic initiators have not found any technical applications. Chemical reactions offer many possibilities for the modification of PVC, but they have been not used on a technical scale yet. Much work has been done on stabilization with nontoxic or metal-free systems. The bulk properties of PVC can be influenced by impact modification through the addition of graft copolymers or by blending with other polymers. Also presented are some problems and recent developments in PVC recycling. © 2003 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 42: 578–586, 2004

Keywords: poly(vinyl chloride) (PVC); history; polymerization; modification; stabilization

INTRODUCTION

Poly(vinyl chloride) (PVC) has been, for more than 70 years, one of the most important polymers, and it is the second most produced thermoplastic resin, placing after polyolefins and before styrene polymers, with a worldwide capacity of more than 31 million tons (i.e., ca. 20% of the total plastic production). Table 1 shows the position of PVC with respect to other plastics and the annual increases of the most important polymer classes. In Western Europe, the PVC consumption in 2000 was about 5.8 million tons.

However, PVC not only has become a big commodity with many applications but also has generally contributed to the development of technical polymer science. For example, peroxides as the first initiators for free-radical polymerization were discovered around 1915 by Klatte during his early experiments on vinyl chloride (VC) polymerization. Polymerization in heterogeneous media was developed with PVC as an example of a polymer not soluble in its own very toxic monomer.

Table 1. Consumption of Plastics Worldwide in 2000 (in millions of tons) and Increases since 1999

Very low-density polyethylene/LLD	29.4 (+4.7%)
High-density polyethylene	21.6 (+4.5%)
Polypropylene	27.7 (+5.4%)
Poly(vinyl chloride)	25.7 (+4.3%)
Polystyrene and EPS	13.4 (+5.5%)
All other plastics	31.6 (+5.5%)

The stabilization of PVC as an extremely heat-sensitive and light-sensitive polymer was successfully introduced on a large technical scale and became an example for the stabilization of many other polymers. Finally, many environmental problems with plastics could be solved and public reservations against chlorine chemistry could be overcome first with PVC.

HISTORY OF PVC

The nearly 170-year history of PVC started in 1835; about 80 years later, the polymer attracted industrial interest, and about 15 years after that, it was commercialized as a homopolymer in the early 1930s (i.e., ca. 70 years ago). A detailed description of the history of PVC, including monomer preparation, polymerization, and processing, was given by Kaufman[1] in 1969. Some important data and milestones are shown in Table 2.

ECONOMIC SITUATION

PVC production on a technical scale started at the end of the 1920s with copolymers of VC and vinyl acetate and with vinyl ethers and acrylic esters. The first technical homopolymerizations of VC were performed between 1930 and 1936 in the United States by Union Carbide and in Germany by IG Farben in Bitterfeld with an annual production of a few hundred tons. The increase in the worldwide capacity and consumption of PVC is shown in Table 3.

Because of the rapid growth of polyolefins in the second half of the 20th century, PVC is the second largest plastic in volume, after polyolefins

Table 2. Milestones in PVC History

1835	Liebig and Regnault discovered VC.
1878	Baumann observed the light-induced polymerization of VC.
1912	Zacharias and Klatte obtained VC by the addition of HCl to acetylene.
1913	Klatte polymerized VC with organic peroxides and described the processing of PVC as a substitute for horn and for films, fibers, and lacquers.
1926	Griesheim-Elektron allowed the PVC patents to lapse; this opened the door for other companies.
1928	Union Carbide and DuPont copolymerized VC and vinyl acetate.
1930	IG-Ludwigshafen copolymerized VC and vinyl ethers and acrylic esters.
	VC was emulsion-polymerized.
	PVC was stabilized with alkali salts.
	PVC was characterized by its K value (Fikentscher).
1932	PVC was chlorinated (IG-Bitterfeld).
1933	Semon used phthalates and phosphates as plasticizers for PVC.
1934	VC was suspension-polymerized (Wacker). The capacity in 1945 was 35,000 tons.
	A PVC pilot plant was opened in Bitterfeld (600 tons/year).
	Frazier Groff (Union Carbide) discovered alkaline earth soaps, and Carbide & Carbon Chemicals used lead salts as heat stabilizers for PVC.
1936	PVC was manufactured by Union Carbide and Goodrich Dialkyl tin soaps were used as stabilizers by Carbide & Carbon Chemicals.
1947	Barium, cadmium, calcium, and zinc soaps were synergistically combined.
1962	VC was bulk-polymerized in a two-stage reactor (in 1975, a one-stage reactor was used) by St. Gobain and Pechiney (Rhone-Poulenc).

Table 3. Production Capacity and Consumption of PVC Worldwide (in millions of tons)

Year	Capacity	Consumption
1939		0.011
1950		0.220
1960	2.0	1.1
1970	7.0	6.6
1980	18.0	11.0
1993	24.7	19.2
1998	27.7	24.0
2000	31.0	25.7

and before styrene polymers (see Table 1). Despite all the technical and economic problems and all the public discussions of the ecology and the environmental dangers and hazards of chlorine chemistry, PVC production has grown for many years worldwide at a rate of more than 4% per year. Two-thirds of all the PVC used today is the rigid type, with its main applications in buildings and construction (pipes, window frames, floor textiles, and rainwater products). Plasticized flexible PVC is used in packaging, medical applications, gloves, toys, cable insulation, and coatings.

SOME RECENT RESULTS

Even after about 70 years of PVC industry, processing, and applications, there are still many new developments and innovations, although only a few of them can be discussed here. The general goal is to lift the economic basis of the production of this rather cheap polymer and to improve the properties of PVC on its way from a commodity plastic to an engineering plastic.

Monomer Production

Most VC has traditionally been obtained by a two-step process, so-called oxychlorination, from ethylene and chlorine. However, EVC (Wilhelmshaven, Germany) has recently developed and now produces in a pilot plant 1000 tons annually in a one-step process from ethene; the advantages include lower energy consumption and reduced emissions. Therefore, a large-scale plant for this process can be expected within the next few years.[2]
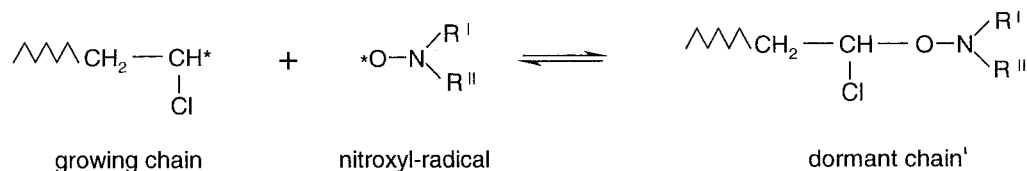
Polymerization

Since its beginning and today, VC is technically polymerized only by free-radical processes in emulsions and suspensions and, more recently, in bulk. The most important process for the production of PVC is free-radical polymerization in an aqueous suspension, followed by emulsion polymerization, by which worldwide about 12–15% of the total PVC production is obtained. Bulk polymerization, technically very interesting, plays only a minor role.

A review of the syntheses and structures of PVC by radical and other polymerization mechanisms was recently made by Endo.[3] This report includes discussions on the terminal and defect structures introduced into the PVC chain during polymerization and on the modification of the structure of PVC by copolymerization and grafting.

In the meantime, it has become possible in the most important heterogeneous polymerization in aqueous media to reduce the residual monomer content of the polymer to a very low level. This is very important for applications in medicine and packaging materials. Moreover, water and energy consumption can also be reduced by new free-radical initiation recipes.[2]

An interesting new development in emulsion polymerization is the use of polymeric tensides as emulsifiers. Such surfactants can be obtained from natural oligomers or polymers by, for example, the partial esterification or etherification of inulin, a carbohydrate with approximately 30–50 D-fructofuranose units, depending on the source. The latex particles produced by emulsion polymerization with inulin tensides are much larger and have a very narrow size distribution in comparison with PVC particles obtained with, for example, sodium dodecyl sulfate under the same conditions. The technical properties of PVC prepared with such high-molecular-weight tensides are still under investigation (cf. ref. 4).

Nevertheless, many attempts to polymerize with ionic initiators such as alkyl lithium[5] or with metal-containing systems such as Ziegler or metallocene catalysts[6,7] have been made, but they have not resulted in industrially useful products and, in some cases, have even resulted in polymers with many deviations from the expected PVC structure. One exception is a type of polymer in which the chlorine atoms are substituted by methyl groups; this is a very expensive route for producing polypropylene from VC.

$\text{CH}_2 - \text{CH}^*$ (Cl) + $^*\text{O}-\text{N} \big\langle {R^I \atop R^{II}}$ ⇌ $\text{CH}_2 - \text{CH} - \text{O}-\text{N} \big\langle {R^I \atop R^{II}}$ (Cl)

growing chain   nitroxyl-radical   dormant chain'

Nitroxyl addition   leads to:

- increased molecular weight

- narrower MW-distribution

- reduced polymerization rate

- re-initiation of other polymers (block copolymers)

Figure 1. Controlled polymerization of VC.

The free-radical polymerization of VC is strongly determined by chain transfer to the monomer. The most important result is that the molecular weight of the polymer is rather independent of the initiator concentration and is regulated, in practice, mainly by the polymerization temperature. Therefore, many attempts to better control the polymerization process have been made, but because atomic transfer radical polymerization (ATRP) is not applicable to some monomers such as VC, other methods of controlling the polymerization reaction are gaining ground. The reason that the presently used ATRP systems of transition metals and alkyl halide initiators do not polymerize monomers such as VC can be seen in the low equilibrium constant of the activation and deactivation steps in the case of monomers that would generate more stable halogen end groups. Here, the formation of too many radicals results in significant termination reactions because of the higher equilibrium constant of the catalyst–monomer pair.[8]

The first metal-catalyzed room-temperature living radical polymerization of VC in aqueous media was recently described by Percec et al.[9] The active Cu(0) catalyst and the Cu(II) species required for the reversible termination step *in situ* proceeds via a self-regulated disproportionation of Cu(I), which is controlled by the nature of the ligand, such as poly(ethylene imine), and provides a solution for the living radical polymerization of VC.

A new way of influencing the polymerization process is nitroxide-mediated controlled free-radical polymerization (CFRP), which shows some advantages. It can also be applied to aqueous systems and is suitable for building up new polymer architectures such as block and graft copolymers, which in some cases cannot be achieved by standard free-radical processes. The polymerization of VC by CFRP is performed by the addition of stable nitroxide radicals in the beginning or during polymerization with the usual free-radical initiators.[10] This limits the number of transfer steps to the monomer and results in higher molecular weights than without nitroxides. A general scheme is shown in Figure 1; the increase in the molecular weight with the polymerization temperature, compared with that of a polymerization not controlled by nitroxide, is shown in Figure 2.

The dormant nitroxide end groups can again dissociate into free-radical chain ends, the chain growth can continue, and the molecular weight distribution of the obtained PVC becomes smaller. There is no remarkable difference in the thermal stability of the polymer with substituted hydroxy amino end groups and that of PVC without such chain ends.

However, the incorporation of nitroxides at the chain ends can be also used for reinitiation processes in the presence of a second monomer such as styrene or *n*-butyl acrylate (Fig. 3). This approach leads to block copolymers that can be applied, such as compatibilizers in PVC blends. An example is the strongly refined morphology of polystyrene/PVC blends by styrene/methyl methacrylate block copolymers.[11] Because of the
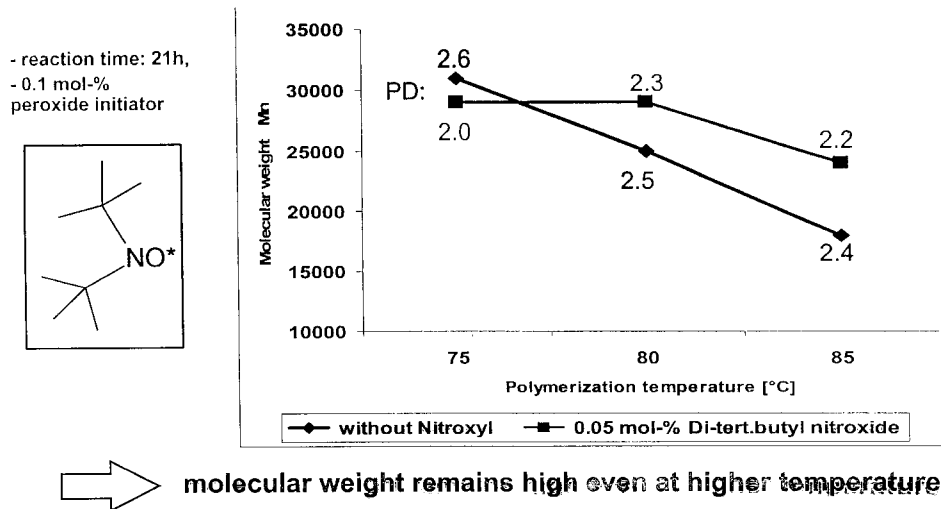
Figure 2.   Influence of nitroxide addition on the molecular weight of PVC.

miscibility of the poly(methyl methacrylate) block with PVC, the modified blends show surprisingly ductile behavior and much higher impact strength than blends without such phase stabilization.

Stabilization

Some of the most serious problems of PVC processing and handling are the rather low thermal stability of PVC, thermal dehydrochlorination beginning at about 100 °C, and discoloration due to the formation of polyene sequences.

During the last 25 years of the 20th century, the most important structural defects in PVC were analyzed, and many questions concerning the initiation step of the splitting-off of hydrogen chloride were solved. However, despite all this effort, as far as the details of these reactions and their contribution to the overall decomposition of PVC, the mechanism of dehydrochlorination is even nowadays not completely understood.

Starnes[12] recently summarized the most important structural and mechanistic aspects. The thermal dehydrochlorination of PVC begins at internal allylic chloride units and at tertiary chlo-
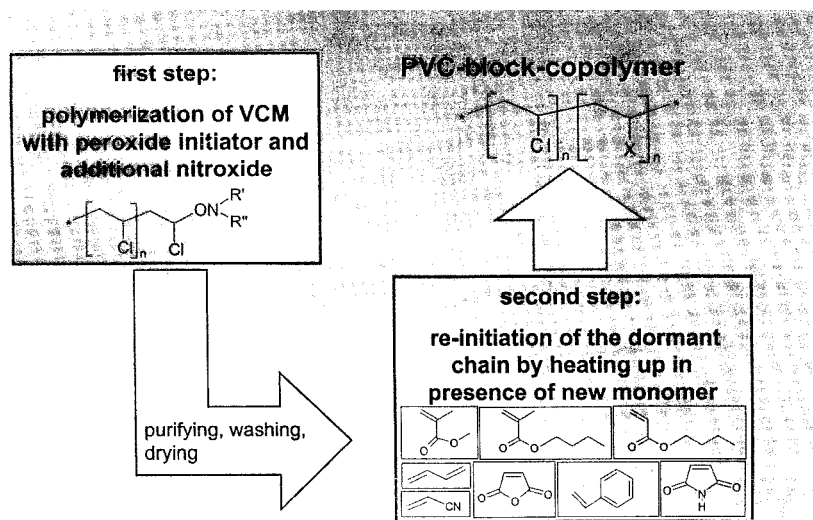

Figure 3.   Block copolymers from nitroxide-terminated PVC.

ride structural defects formed during polymerization associated with short or long chlorinated branches. The sometimes discussed carbonylallyl structures and the tacticity are unimportant as initiators of thermal dehydrochlorination. Both the initiation and subsequent formation of conjugated polyene sequences occur via carbenium chloride ion pairs or by a concerted four-center quasi-ion route. Pathways with free radicals are involved in polyene elongation. Cyclization reactions seem likely to contribute to the termination of polyene growth.

Long before these mechanistic studies were performed, it was found very early in the beginning of the PVC industry that a number of chemicals could be used as stabilizers against these very undesirable degradation processes. In the beginning of the commercialization of PVC, alkali and some organic bases such as urea were used as heat stabilizers before Frazier Groff (Union Carbide) in 1934 discovered alkaline earth soaps for PVC stabilization. Since then and until now, lead salts (discovered at Carbide & Carbon Chemicals) have become increasingly important as stabilizers. A new field started with the development of dialkyl tin soaps at Carbide & Carbon Chemicals in 1936. A great deal of progress was initiated by the synergistic combination of barium, cadmium, calcium, and zinc soaps in 1947 and by dibutyl tin thioglycolates by Eliot Weinberg (Metal & Thermit Corp.) in 1952.

The basic principles of PVC stabilization against heat and light were developed between 1930 and 1950, but the search for more effective, less toxic, and environmentally friendly stabilizing systems is one of the most important tasks of the PVC industry. All stabilizers have the same functions: to neutralize the released hydrogen chloride and to prohibit further degradation by preventive or curative reactions.

Meanwhile, the stabilization of PVC has become a large market, with about 850,000 tons in 2001. Lead, despite all the discussions about its toxicity, is still the most used PVC stabilizer (Table 4). Presently in Europe, about 112,000 tons of lead are used annually, but because of safety and legal regulations in many countries, in 2010 a reduction to about 80,000 tons is expected.[13] The most important substitute will be calcium/zinc systems in combination with organic costabilizers based on polyols or phosphites.

For technical use in most cases, various chemicals must be combined in stabilizer packages because each individual product alone has no suffi-

Table 4. Consumption of PVC Stabilizers in Europe in 1998 (in tons)

Lead	120,000
Organotin	15,000
Mixed metal	15,000
Cadmium	0,05
Light stabilizers	6,000

cient stabilizing effect under the processing conditions. For instance, mixed metal stearates such as modern calcium/zinc stabilizers have to be supported by polyols or epoxidized oils as costabilizers. Because in such recipes with PVC at least technically compatible polymethacrylate recipes are usually added as lubricants, methacrylate-based copolymers with 2-hydroxyethyl or 2,3-epoxypropyl methacrylate are combined with costabilizing lubricants or lubricating costabilizers[14] (Fig. 4).

Such functional copolymers improve the thermal stability and show a strong costabilizing effect on calcium/zinc-stabilized PVC, the effectiveness increasing with increasing hydroxy or epoxy group content.[4,15] Because of this costabilizing effect, in some cases, the concentration of metal-containing stabilizers can be reduced by 25–50%. Moreover, the multifunctional copolymers exert a positive influence on the plasticizing behavior, the die swell in the extrusion of profiles, and some other processing properties. They do not cause any fogging or increases in volatiles or deposits on the product surface such as low-molecular-weight epoxides or polyols, even though these copolymers on a molecular level are immiscible with PVC.[15]

Another actual development in the field of stabilizers is metal-free organic compounds [i.e., organic-based stabilizers (OBSs)]. As early as the 1930s, some organic bases such as urea, diphenyl guanidine, aliphatic amines, and indol and thiourea derivatives were proposed as PVC stabilizers, but they were soon substituted by the aforementioned and more effective metal-containing stabilizers. Because of environmental discussions on such metals, interest in organic stabilizers has recently been growing.

Some of these compounds are shown in Figure 5. In practice, they have been combined with HCl acceptors, costabilizers such as polyols, antioxidants, and lubricating agents. Recent investigations have shown good effects in the stabilization of profiles and pipes with about 2.5–4 phr OBS.[16]

Not much is known about the mechanism of the stabilization process by these systems, but it

Costabilizers

♦ Low molecular compounds
♦ Functional groups
  ♦ Polyols
  ♦ Epoxides

Processing aids

♦ Polymers
♦ Wall sticking polymers
  ♦ Polymethacrylates

Copolymers from methyl methacrylate and monomers with functional groups

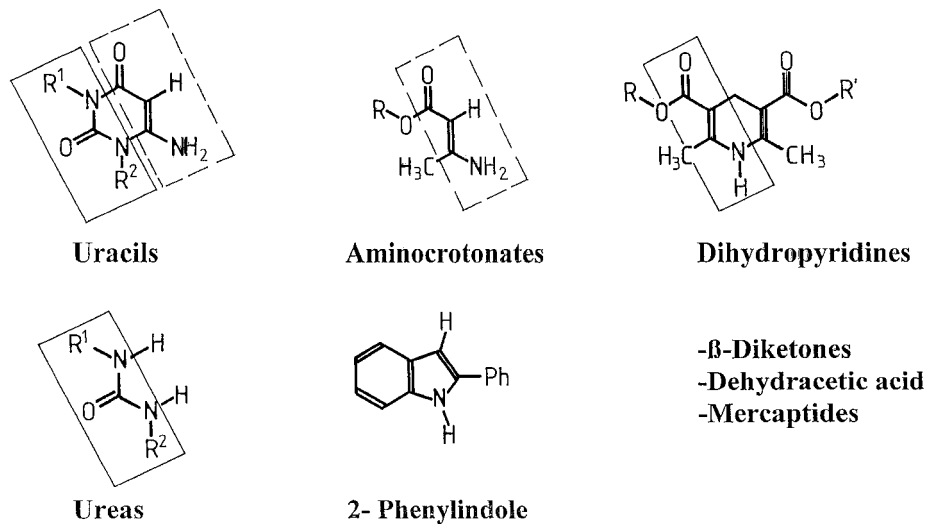| Polyols	Epoxides
2-Hydroxyethyl methacrylate (HEMA)	2,3-Epoxypropyl methacrylate (EPMA)
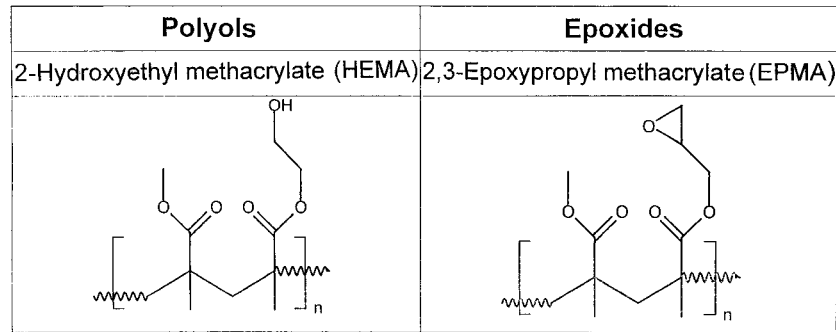
Figure 4. Polymeric costabilizers for PVC.

is proposed that the stabilization is caused by a substitution reaction of labile chlorine atoms in PVC by stable groups of organic compounds with acidic hydrogen atoms under the elimination of hydrogen chloride. Therefore, these systems require the addition of HCl acceptors[16] (Fig. 6). It can be expected that such OBSs will find increasing importance during in the future.
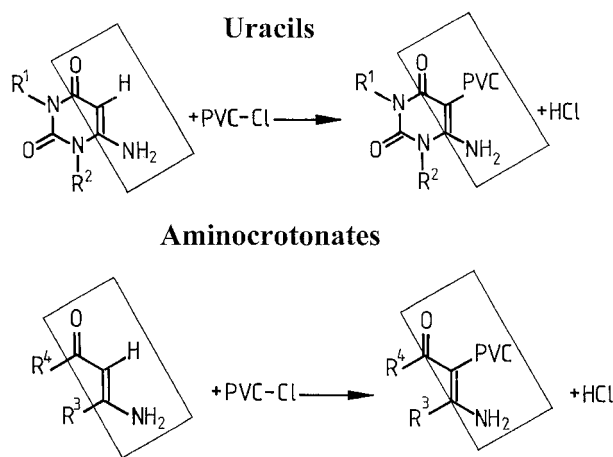
Another class of nonmetallic additives for the thermal stabilization of PVC is the new organic thiols, which were described recently by Starnes and coworkers[17,18] (Fig. 7). They can be used in the absence of metal-based additives. When they are introduced at high loading levels, they also function remarkably well as PVC plasticizers.

Recycling of PVC

During processing and at the end of the service life of PVC articles, large amounts of scrap arise. As landfill capacities in most countries are limited, land-filling as a disposal process is increas-

Uracils

Aminocrotonates

Dihydropyridines

Ureas

2- Phenylindole

-ß-Diketones
-Dehydracetic acid
-Mercaptides

Figure 5. OBS for PVC.

Uracils

Aminocrotonates

Figure 6. Proposed reaction mechanism for the co-stabilizing reactions of PVC with OBS.

ingly seen as the last option. Incineration, another method of disposing of solid waste, presents, in the case of PVC, many technical and environmental problems because of the high chlorine content of the polymer and the large amounts of hydrogen chloride that are emitted during thermal decomposition. Therefore, many techniques for the material and chemical recycling of PVC have been developed during the last 15 years.[19,20]

For the material recycling of PVC from municipal or industrial solid waste, many proposals have been made, and some of them have been realized, especially in Germany and when relatively large amounts of similar waste products are available and can be collected (e.g., roofing materials, floor coverings, and window frames).

A very promising method is the so-called Vinyloop process. This process was developed by Solvin in a joint venture with some PVC processing companies and was supported by European PVC associations. It separates PVC from other materials such as metals, textiles, or glass fibers [e.g., in cable (copper), foil (aluminum), floor coverings, or tarpaulins].

In a plant in Ferrara, Italy, with a capacity of 10,000 tons, shredded PVC waste is dissolved in a mixture of organic solvents such as methyl ethyl ketone with some other solvents. In a second reactor, steam is added to this solution to precipitate PVC, and the solvent is separated as an azeotrope with water, from which the organic solvents can be recovered. The obtained PVC granules are compounds containing the additives of the used PVC waste, such as stabilizers and fine filler particles. It is said that the process will be

economically feasible if the obtained new compound can be sold for about 50 Eurocents per kilogram.[21]

Furthermore, the chemical recycling of waste PVC by slag bath gasification has recently been attracting increasing interest. It is based on the idea of converting used PVC back into chemicals for monomer synthesis or other petrochemical processes. A pilot plant with a capacity of about 2000 tons per year for slag bath gasification was started recently in France to produce hydrogen chloride and a mixture of carbon monoxide and hydrogen, which can be used as syngas. As far as we know, because of technical and economic problems, this process will not be transferred into a commercial one.

OUTLOOK

A review of about 70 years of industrial PVC shows many generally important contributions to polymer science and technology. During the past 20 years, most environmental problems could be solved, and public reservations against chlorine chemistry could be overcome.

However, there are many future demands, so long-term research and development by the PVC industry is necessary to confront the global economic problems of the plastic industry (e.g., the need for nontoxic, metal-free stabilizers). Another urgent technical task is the search for nontoxic plasticizers to avoid the danger of substituting
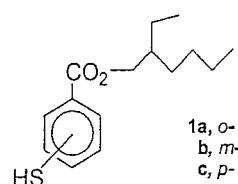
Mechanism of Stabilization:

$$RCl + 2R'SH \longrightarrow RH + R'SSR' + HCl \qquad (1)$$

$$RCl + R'SH \longrightarrow RSR' + HCl \qquad (2)$$

HCl can be neutralized with epoxidized soybean oil

Figure 7. Plasticizer thiols (according to ref. 17).

Table 5.   Future of PVC[a]

	2000	2010
Increasing standard-of-living per capita consumption (kg) of plastics worldwide (Western Europe, 92 kg; and United States, 105 kg, in 2000)	24.5	37
Growing plastic consumption worldwide (in millions of tons)	180	250
PVC consumption worldwide (in millions of tons)	25.7	37.5

[a] Conservate estimates are given that do not consider the growth of the global population or new fields of application.

other polymers, such as thermoplastic elastomers, for PVC. Also, the development of new PVC types with improved properties, by grafting or blending, for example, to make an engineering plastic from a commodity should be important to the future of the PVC field.

Another necessity, at least in Europe, is to better inform the public by more demonstrations of product recyclability and success in reducing environmental pollution. In public discussions of the problems of chlorine chemistry, it should be taken into consideration that PVC is a large chlorine trap because it consumes a high fraction (nearly 30%) of the total chlorine production as a byproduct of caustic soda.

In conclusion, PVC should be seen as an inorganic–organic hybrid polymer because of its nearly 57% chlorine content. It owes many of its interesting properties such as flame retardancy, resistance to most common solvents, polarity, and compatibility with many additives (not only plasticizers and stabilizers but also various kinds of fillers) to the presence of its inorganic component.

If there are no new applications of PVC in the near future and if PVC is not substituted by other polymers on a large scale, only because of the increasing standard of living in developing countries, PVC consumption worldwide will grow from about 26 million tons per year to 37 million tons in 2010 (Table 5).

If all these inherent capabilities of this old polymer are used, PVC can by no means be considered a "ripe" plastic, and we can expect further growth in the future. Therefore, we should remember what the unforgettable Herman Mark[22] said in his preface to the *Encyclopedia of PVC* with respect to PVC:

> Old soldiers never die—they just fade away.
> Old plastics never die—they hang on and stay.

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