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Trends in Industrial Polymer Research

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Summary: In the past decades a shift in paradigm took place in industrial polymer research for structural materials. Only a few new polymers based on new monomeric building blocks were developed. The main focus is now on tailoring improved "old polymers" with well-defined structure and properties based on a set of low cost "old" monomers using controlled polymerization mechanisms.

Kewords: controlled polymer synthesis, industrial polymer research, modification and improvement of polymers, structural polymers

1 Overall Economic Background

Some one hundred years after they were first synthesized industrially, and eighty years after their molecular structure was solved, synthetic polymers continue to play an important role satisfying the material needs of today's society in the areas of diet and nutrition, health, accommodation, clothing, communication and mobility. The demand for polymers has rapidly grown over the last decades to generate a world market volume of 154 million metric tons in 2001. The secret of the success of structural polymers is to be found in their unique combination of hardness, lightness, resistance to corrosion, flame-retardant properties, weathering resistance, stiffness and toughness. In terms of production volume, structural synthetic polymers have overtaken steel in the last twenty years. The consumption per capita exhibited an extraordinary growth despite the two oil crises compared to other materials like wood or steel (Figure 1, example USA).

In defiance of this growth the margins for polymers have declined by 40 – 60% within the last decade due to over-capacities and severe competition (Figure 2). As a consequence a dramatic concentration process took place in industry. The capacities of world scale single strand plants have steadily been increased to reduce specific costs reaching 400 kt/a for polypropylene (PP) nowadays.

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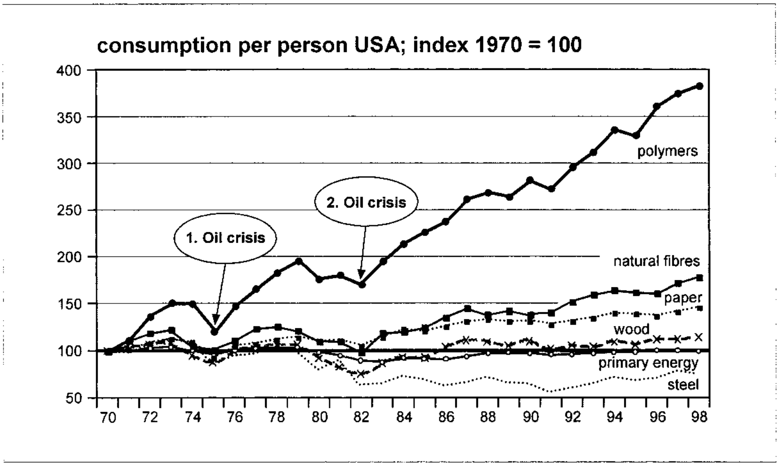


Fig. 1. The development of the demand per capita for different materials in the USA.

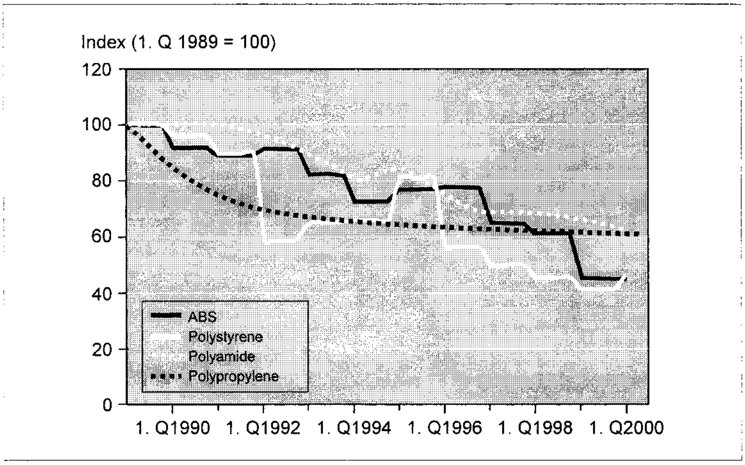


Fig. 2. Trends in margins for commodity polymers.

Many of the commercially most important classes of polymers were first manufactured industrially decades ago. Polystyrene (PS) and polyvinylchloride (PVC) both 70 years ago, polyethylene (PE) 60 years ago. Only a few commercially relevant polymer classes have been introduced within the last 40 years. In terms of volume, the four largest classes of synthetic polymers (PE, PP, PVC and PS) represent over 85% of the world market (Figure 3), a fact that is in sharp contrast to the predictions of the past.

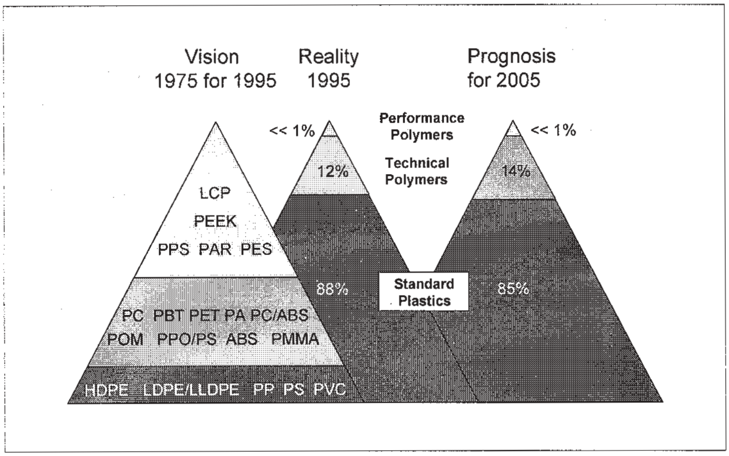


Fig. 3. Vision and reality of market development of thermoplastics within the last 25 years.

Seen the economic difficulties and the mature character of the involved polymers the question arises what the important drivers of the future will be in order to ensure a profitable business with polymers.

2 New Polymers from New Monomers

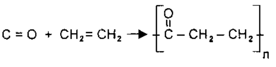
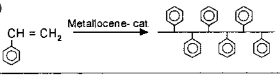
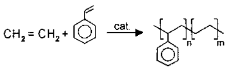
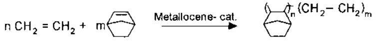
Do we really need new monomers to achieve new polymeric materials to fulfil customers' needs? The answer is quite clearly "no". The number of polymers based on new monomers decreased significantly in the last decade and such polymers only play a role in niche markets.

3 New Polymers from Old Monomers

In place of introducing new monomers it is more attractive to obtain new polymers by known "old" monomers. Due to the tremendous progress in catalyst design existing cheap monomers could be combined to new polymers with new structures achieving properties similar to engineering plastics. Several examples can be found during the last years (Table 1):
Are these new polymers from old monomers really successful in the market? After 20 years of intensive R&D efforts, and 5 years after the market launch, SHELL[1] has given up the development of polyketones.

DOW also announced to withdraw its interpolymers from the market.[2] SPS and COC are still being produced in semi commercial plants but growth rates are far smaller than forecasted.[3]

Table 1. New polymers from old monomers.

Polymer Trademark	**competitive material**	**pros**	**cons**
Polyketone Carilon® (Shell) Ketonex® (BP)  $C=O + CH_2=CH_2 \rightarrow \left[\overset{O}{\overset{\Vert}{C}} - CH_2 - CH_2 \right]_n$	Polyamide Polyacetal Polyethylene	toughness, chemical resistance, barrier properties	processing stability, property deterioration by fillers
Syndiotactic Polystyrene (sPS) Xarec® (Idemitsu) Questra® (Dow) 	Polybutylene terephthalate	low density, no shrinkage, no hydrolysis	toughness, long-term service temperature
Ethylene/Styrene Interpolymer (ESI) Index® (Dow) 	EVA S/B block copolymers flexible PVC	broad spectrum of properties, no outstanding single characteristic	
Cyclic Olefin Copolymer (COC) Topas® (Ticona) 	Polycarbonate, Polymethyl-methacrylate	transparancy, moisture barrier, good electrical insulating property	costs, toughness-stiffness ratio

At first sight, new polymers from old monomers can be attractive since raw material costs are rather low. New polymerization technologies and new catalysts, however, have to be developed and implemented. Simultaneously, applications and processing at the customer side have to be worked out. These cost- and time-intensive procedures have often been underestimated.

A possible explanation can provide Figure 4, the so called "learning curve" that is simply based on an empiricism but holds for sewing machines as well as carbon fibers. The learning curve predicts that by doubling cumulative production a cost reduction of 20 – 30% is achievable simply by becoming more experienced with the product. Each new polymer, although having the potential to be lower in cost, is at the starting stage much more expensive than an existing polymer that is produced in millions of tons and therefore much further down on the learning curve.

One might come to the opinion that these new polymers simply have the fate to be too late on the marketplace to be successful.

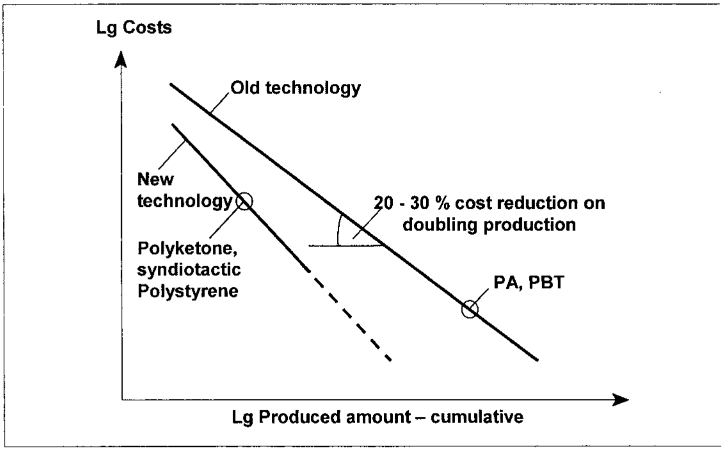


Fig. 4. The “learning curve” (explanation see text).

One example of the few new polymers, derived from a known monomer, that have been placed successfully on the marketplace is linear low density polyethylene (LLDPE). UCC licensed its technology aggressively from the beginning on, and a lot of licensees helped to ride down the learning curve.

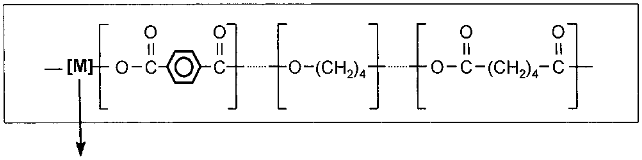
4 Improved Old Polymers

A question that naturally arises from all these facts is whether we really need new polymers? We are convinced that the potential of the existing polymers is by far not yet exhausted considering the tremendous progress in polymer science. In particular the progress has been manifested by:

- An improved understanding of the relationship between primary and higher-order structures of synthetic macromolecules and the desired physical and applications-related material properties.
- The development of reaction conditions to achieve the controlled polymer synthesis for almost all different polymerization processes as well as for a large number of monomers to create macromolecules with specially tailored structures. Related to this is the development of catalysts of even higher selectivity and even greater efficiency.
- Exploiting the methods of high-throughput synthesis, high-throughput screening and data management to significantly accelerate research in these areas.

Based on this knowledge, each improvement of existing polymers, so called “drop in solutions”, are by far easier to implement and commercialize. Many examples by BASF can be found:

1. Based on market studies BASF’s researchers had the goal to develop a biodegradable film grade material with LDPE-like properties for packaging applications. As for this application price is decisive our strategy was to develop a biodegradable polymer based on existing monomers with existing technology in existing plants. In the end the problem solution was to modify PBT by adding the aliphatic adipic acid and to improve properties by branching and chain extension (Figure 5), so all in all quite conventional methods.[4]



M: Branching and Chain Extension

- Random copolyester based on:
  - terephthalic acid
  - adipic acid
  - 1,4-butane diol
- Tailor-made structures based on a modular system **M**

Fig. 5. Improved old polymers: Ecoflex® – a biodegradable “poly(butyleneterephthalate)” (PBT).

However, we obtained a 100% biodegradable polymer (Ecoflex®) with LDPE like properties that can be used as garbage bag, cling film or biodegradable cover sheet for lunch boxes out of starch.

2. Key for polyamide 6 fiber applications in textiles or carpets is the UV stability. We could show, that attaching the additive to the chain end rather than just simply blending it with the polymer is much more efficient because there is no loss of stabilizer during processing and life time of the product.[5] Most efficient are HALS- (hindered amine light stabilizers) type stabilizers that are incorporated into the chain during the polycondensation by chain end capping.

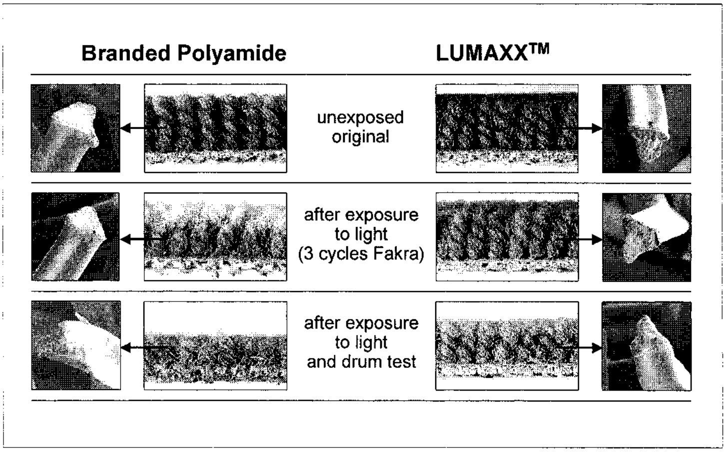


Fig. 6. Change of appearance of fibers after testing.

Figure 6 illustrates the effect of such attached additive in comparison to conventional polyamide. Our new material shows better color fastness and the pile height is much less reduced after usage because of the unique stabilization. Conventional carpet fibers get brittle and break leading to “walking streets”.

3. The addition of magnesium or aluminum alkyls to butyllithium, forming an “ate”-complex, allows to slow down the anionic polymerization of styrene to same rates as the radical polymerization. It could be shown by BASF[6, 7] that up to 180 °C and in bulk this so called retarded anionic polymerization of styrene is still first order and living (Figure 7).

   This enables us to produce high impact polystyrene (HIPS) anionically in existing radical HIPS plants under same conditions (drop in solution) with reduced level of residuals, with similar or even improved properties. The higher costs for initiator and solvent purification can be compensated by an integrated rubber production.

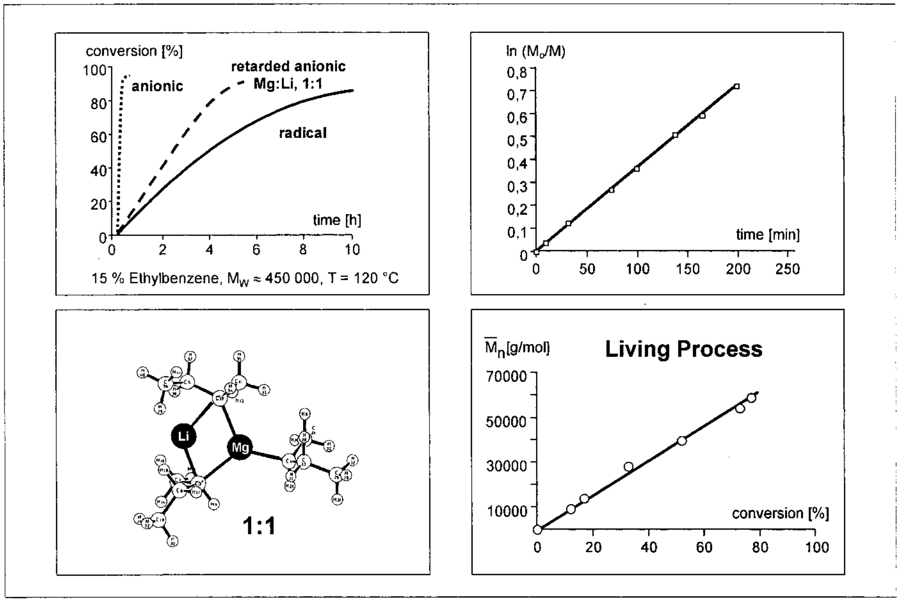


Fig. 7. Retarded anionic polymerization: kinetic data and proposed structure of the Li-Mg-"ate" complex.

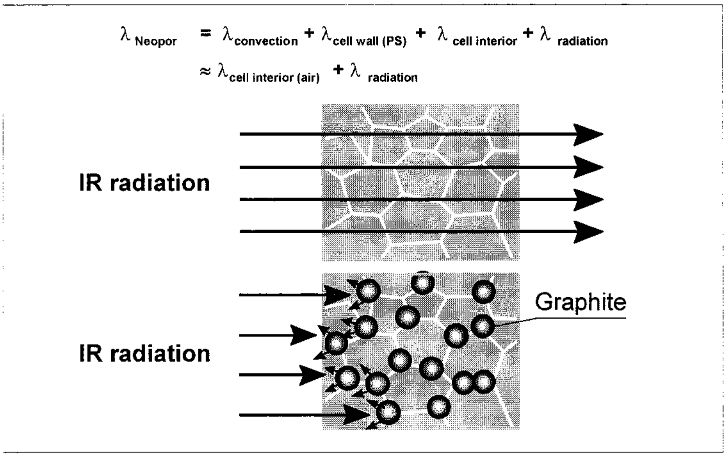


Fig. 8. How Neopor® cellular foam works.

4. A simple way of improving properties of existing polymers is by adding fillers from micro- down to the nano-scale. By adding graphite to expandable polystyrene it is possible either to reduce thickness of sheets by 30% at densities between 10 - 15 g/l to get

the same insulation properties compared to conventional Styropor® or to reduce the density of Neopor® by 50% compared to standard Styropor®.[9]

The IR radiation as a main contributor to the heat conductivity is reflected by the graphite particles that otherwise would penetrate the insulation foam almost without hindrance (Figure 8).

5. Integrated system solutions also allow new applications and growth potential for known polymers.

   High off-line coating costs and/or expensive polymer blends for on-line coating have still limited the usage of plastic panels in automotive applications. BASF is developing a new concept of *Paintless Film Molding* (PFM; Figure 9) to significantly reduce costs:[9] A three layer coextruded and pigmented foil is backed by injection molding of glass reinforced ASA, ABS, PA, PBT or blends there of. By this new technique expensive coating costs are saved and cheap backing material can be used. The key is that the materials exhibit good compatibility to result in good adhesion to each other.

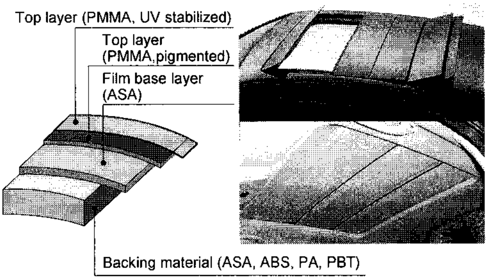


Fig. 9. Paintless Film Moulding (PFM).

These five examples demonstrated innovative solutions to further expand the potential of the old polymers. We are steadily improving properties while lowering the costs that is the key factor for further growth.

5 Outlook

The tremendous progress in catalyst research has led to new polymers with even lower potential manufacturing costs. Nonetheless, the effect of economy of scale, underestimated costs for processing and application development, the huge data base of the existing polymers to be developed for new polymers and also the progress of the old polymers will limit their success. New business models are necessary as the example of LLDPE has shown.

On the other hand, the progress in polymer science will bring us closer to the ultimate vision of "retro-synthesis":

- A deeper understanding of structure/property relationships permits to translate properties into morphologies and molecular structures.
- Such polymers are then tailored by more advanced methods of controlled synthesis (Figure 10).

As a consequence the conventional way of trial and error will become obsolete.

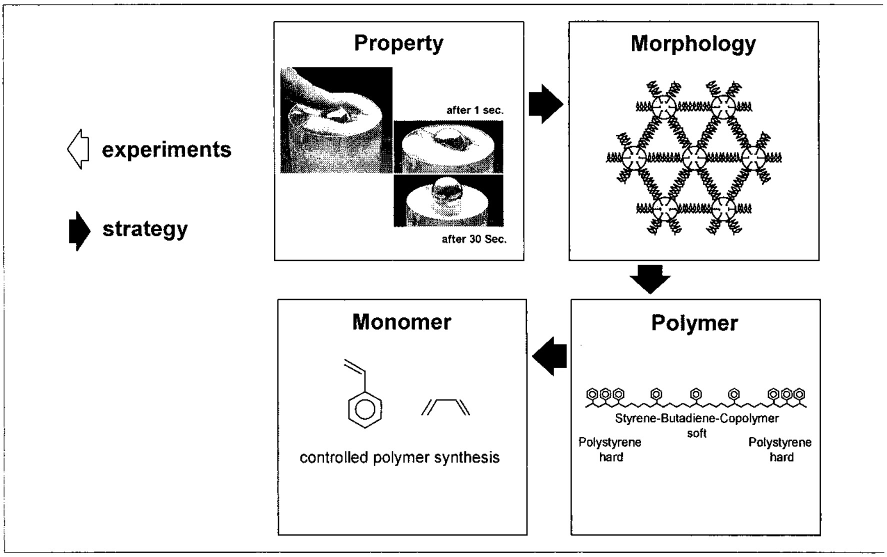


Fig. 10. The vision of polymer retro-synthesis.

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