DOI: 10.1002/masy.200650824

Anionic High Impact Polystyrene: A New Process for Low Residual and Low Cost HIPS

Desbois Philippe,[*1] *Warzelhan Volker,*[1] *Niessner Norbert,*[1] *Deffieux Alain,*[2]
Carlotti Stephane[2]

Summary: BASF has developed a new process for the manufacturing of High Impact Polystyrene (HIPS) via an anionic route: the so-called A-HIPS process. The driving forces were the development of a product with a low content of residuals and improved cost performance compared to the radical state of the art HIPS. The production of A-HIPS includes the synthesis of the rubber, a styrene-butadiene block copolymer. To overcome the main challenges of anionic polymerization such as reactivity control, solvent purity and initiator costs, BASF has developed its own proprietary technology, the Retarded Anionic Polymerization (R.A.P.) which allows styrene polymerization to 100% conversion under similar reaction conditions as the radical polymerization. A new low cost anionic initiator system (BuLi-free), based on sodium hydride and triethylaluminum, has been developed for perfect reactivity control over a broad temperature and concentration range even up to bulk conditions.

Keywords: anionic polymerization; living polymerization; polystyrene; processing; retarded anionic polymerization (R.A.P.)

Introduction

Polystyrene is one of the most important thermoplastics in the world. Though styrene can be polymerized by all the known methods for vinyl monomers, commercial polystyrene production is still based on a free radical mass polymerization process as outlined 70 years ago [1, 2]. Even though anionic styrene polymerization has been known since that time [3] and allows the control of the molecular architecture in a much wider range leading to polymers with tailor-made property profiles, it is commercially used only for niche products because of the associated high production costs (e.g. solvent and monomer purifications, initiator costs).

Conventional, butyllithium initiated styrene anionic polymerization faces several drawbacks. At high monomer concentrations, turnover rates are exceedingly high, and removal of the heat of polymerization is difficult. Furthermore, at high temperature, side reactions occur and a decomposition of the propagating carbanions is observed.

Hence, anionic polymerization has so far been restricted to diluted solutions and low temperatures (<60 °C). Under these conditions, general purpose or high impact polystyrene cannot be produced economically. Nevertheless, we believe that living anionic polymerization is a suitable tool for the synthesis of innovative materials that improve properties of the polystyrene family. The question is: how to conduct a controlled anionic polymerization under similar conditions as the radical process?

High Impact PS consists of a PS matrix which brings stiffness and a soft phase which improves the toughness of the brittle PS. Tuning of molar masses, polydispersity index and lubricant content on the one hand, as well as rubber content, rubber particle diameter, degree of branching and

---

[1] BASF AG, Polymers Laboratory, D-67056 Ludwigshafen, Germany
Fax: (+49) 0621 60 20313
E-mail: Philippe.desbois@basf.com

[2] LCPO, University Bordeaux-I, avenue Pey-Berland, 33402 Talence, France

crosslinking on the other hand, allows optimization of the main properties of HIPS, namely: flowability/heat resistance/stiffness: toughness ratio/stress cracking resistance or gloss (Figure 1). The main applications of this product are injection molding for electronic housings and thermoforming for fridge in liners or food packaging.

At BASF, a vessel/vessel/tower/tower reactor configuration is used with a degassing unit (Figure 2). Firstly, polybutadiene bales are solubilized in a styrene/ethylbenzene mixture. Then styrene is polymerized in the vessel reactors, in presence of peroxide initiators, up to the formation of rubber particles in the PS matrix. The cohesion between polystyrene and polybutadiene phases and the good property profile of this material result from the grafting of polybutadiene chains with PS, leading to the so-called salami morphology. The tower reactors work at higher temperatures to complete the reaction. However, due to many side reactions, a final conversion of only 80% is achieved. 20% of the unreacted monomer has to be removed before pelletizing. As a result, the polymer may contain several hundred ppms residual styrene.

In order to improve the final conversion and to lower the residual styrene content we have aimed to use the potential of the controlled anionic polymerization. It is known that this process allows 100% monomer conversion, with a final polymer containing less than 10 ppm residual styrene. Besides, the anionic polymerization leads to a polymer chain with a more stable molecular structure; with no head to head placement of the phenyl groups, which limits chain breaking and monomer regeneration during processing. In addition, much less oligomers are formed during the anionic polymerization. We could also argue that since the rubber is made by anionic polymerization, why not make the whole HIPS process anionic? But, so far, it was assumed that the anionic route is too expensive due to solvent purification, initiator costs and the absence of a drop in solution due to the high activity of this polymerization necessitating reactor redesign. The driving force of this project was the development of a low residual product with improved cost compared to its radical counterpart while maintaining product performance.

Discussions

The technology of ‘‘living’’ anionic polymerization has been used for almost 20 years by BASF to produce styrene-butadiene block copolymers like Styrolux® and lately Styroflex®. Attempts to transfer this powerful method to GPPS and HIPS were impeded by the excessively high reaction rates that required the use of dilute solutions. In contrast, for the radical process it is straightforward to maintain the polymerization at the desired value (Figure 3). The anionic route leads, in bulk or at high temperature, to a run-away reaction. As a result, high temperatures - more than 400 °C in case of bulk polymerization - are reached leading to the non-control of the

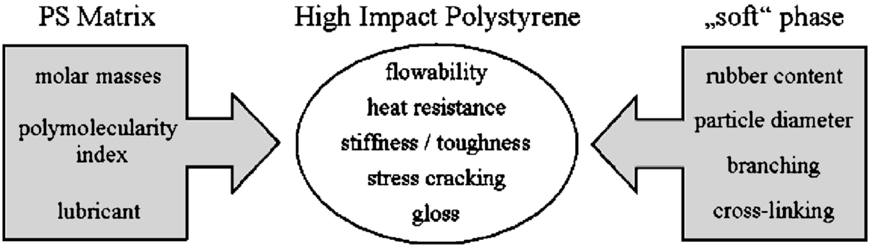


Figure 1.
Main features of the PS matrix and the soft phase enabling fine-tuning of the main properties of high Impact Polystyrene.

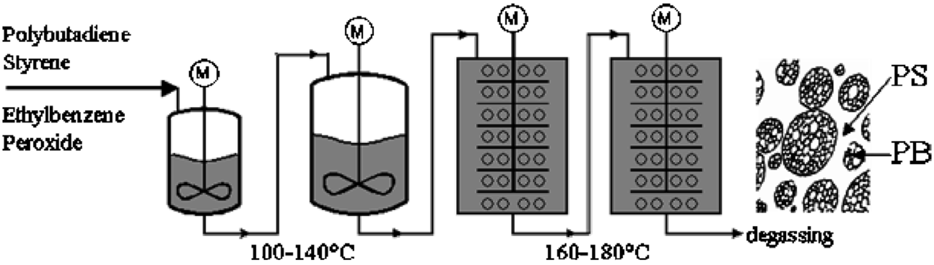


Figure 2.

BASF R-HIPS process: vessel-vessel-tower-tower reactor configuration, including electron microscopy of an R-HIPS sample stained with OsO_4; white domains: polystyrene (PS), dark domains: polybutadiene (PB).

reaction and to the degradation of the system. However, we feel that the key to commercial success of anionic PS lies in the ability to manufacture it within the existing free radical polymerization conditions. To this end, the only solution is to reduce the reactivity of the active centers.

The anionic polymerization of styrene is initiated, as a rule, by RLi derivatives. Under normal conditions, the process can be considered as living (absence of termination and transfer reactions). In apolar solvents, monomeric PSLi species are in equilibrium with PSLi dimers (Figure 4). This latter species are present in a very large proportion whereas the very small fraction of monomeric species is considered to be active. Nevertheless, a fast exchange between both species allows the homogeneous growth of all PSLi chains. Equilibrium between active and dormant species is an important tool to decrease the reactivity of the system, although it is not sufficient in the present case to reach our goal.

Another way to decrease the intrinsic reactivity of the propagating active PSLi species was therefore investigated. It has been shown that some organometallic derivatives, such as Lewis acids, can induce hybridization of the C–Li bond via bimetallic complexation (Figure 5). Li, Mg, Al, B and Zn derivatives can form such types of complex in which each alkylithium is coordinated by an alkylbridging group via electron deficient bonding. This so-called

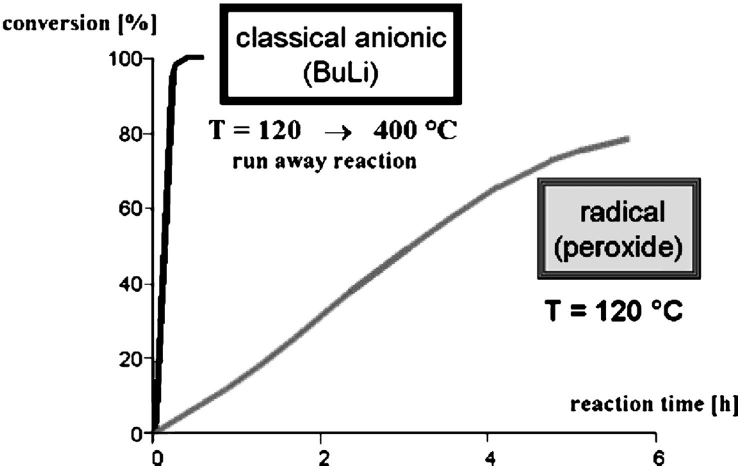
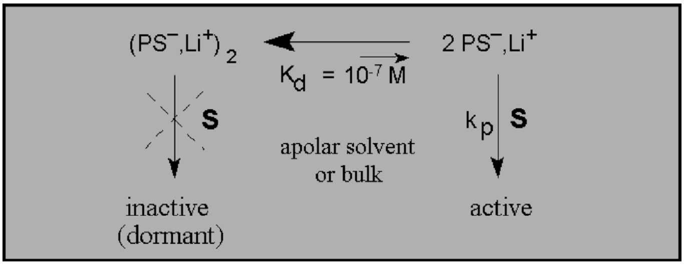


Figure 3.

Conversion versus reaction time for a classical anionic (BuLi) and a radical styrene polymerization, 15% Ethylbenzene, $M_W = 450\,000$, $T_{start} = 120$ °C.



$$V_p = \underbrace{k_p \cdot K_d^{1/2}}_{\mathbf{k}_{app}} \cdot [PSLi]^{1/2} \cdot [S]$$

Figure 4.
Anionic polymerization of styrene in an apolar solvent.

"ate" complex has a strong effect on the reactivity. It has been already shown [4] that the addition of organometallic Lewis acids such as dialkylmagnesium or trialkylaluminum to the anionic styrene polymerization permits the control of the rate of polymerization over a large temperature range. The overall turnover can be adjusted to enable a hitherto unseen controlled anionic mass polymerization.

Using this new technology named "Retarded Anionic Polymerization", the overall reactivity can be perfectly tuned over broad monomer concentration and temperature ranges simply by adjusting the Mt/Li ratio. Indeed, retardation of the polymerization permits the control of the reaction kinetics, thus allowing a good removal of the polymerization heat (Figure 6). The appropriate Mt/Li ratio depends on the associated metal and reaction conditions: 2–10 for the $Bu_2Mg/BuLi$ system or 1–2 if the derivative contains one special Mg–O bond whereas it is generally less than 1 with the aluminum derivatives, except compounds containing Al–O bonds. Hence, it is possible, for the first time, to run a controlled anionic styrene bulk polymerization. This gives us the possibility to synthesize high impact polystyrene with highly innovative properties linked to the anionic process (no residual styrene, control of the reaction, living propagating species, . . .).

The influence of $i\text{-}Bu_3Al$ on the kinetics of styrene polymerization initiated by s-butyllithium was firstly investigated in cyclohexane at 50 °C (Figure 7). The plot of the k_{app} of the reaction versus the Al/Li

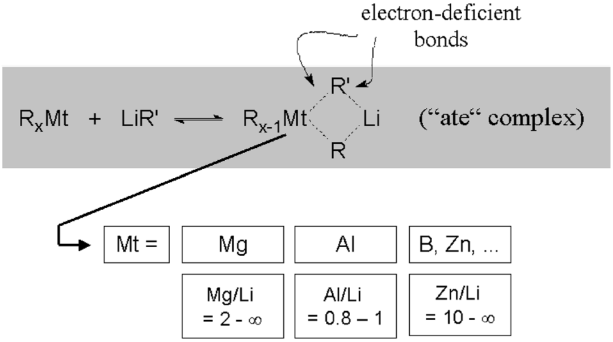


Figure 5.
Concept of Retarded Anionic Polymerization and necessary Mt/Li range to reach an appropriate reactivity control.

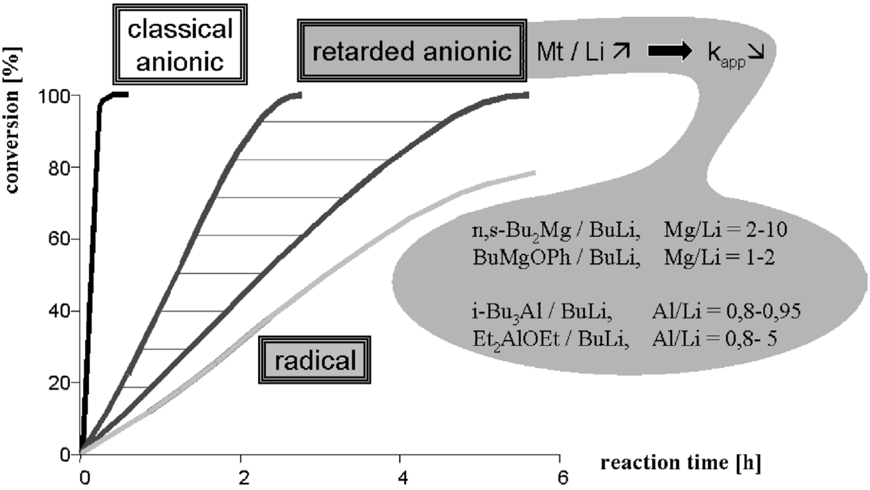


Figure 6.
Conversion versus reaction time for a classical anionic (BuLi), retarded anionic and radical styrene polymerization, 15% Ethylbenzene, $M_W = 450\,000$, $T_{start} = 120\,°C$ (Mt/Li range to reach an appropriate reactivity control).

ratio, can be divided into 3 distinct regions, from 0 to about 0.8 the k_{app} slightly drops; when the ratio Al/Li get close to 1, the reactivity sharply decreases and at ratio equal to 1, the polymerization is totally inhibited. For example, a 500 fold decrease of the apparent rate constant of propagation is obtained at a ratio of 0.85 with still a perfect linear progression of the Ln Mo/M versus time.

Experimental molar masses increase continuously as the reaction proceeds (Figure 8a) and are in agreement with theoretical ones assuming one chain per lithium species. This indicates that only Li species are active and the polymer distribution is still narrow (PDI < 1.1 at 50–100 °C). The linear evolution of k_{app} versus time (Figure 8b) shows that there is no termination during the polymerization, the linear

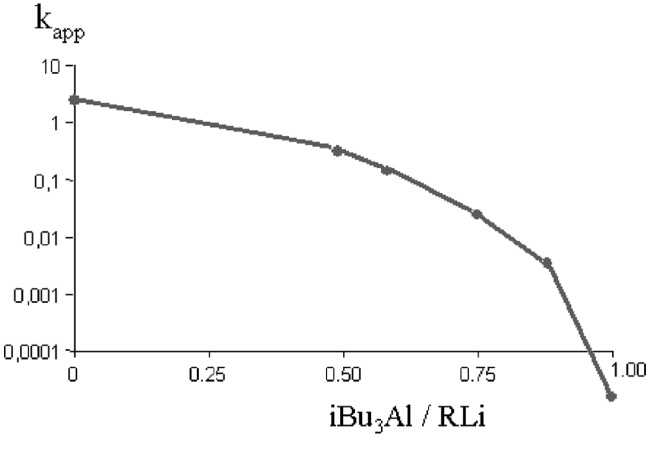


Figure 7.
Apparent rate constant of propagation (k_{app}) of the styrene polymerization initiated by s-BuLi versus iBu_3Al/RLi ratio, cyclohexane, 50 °C.

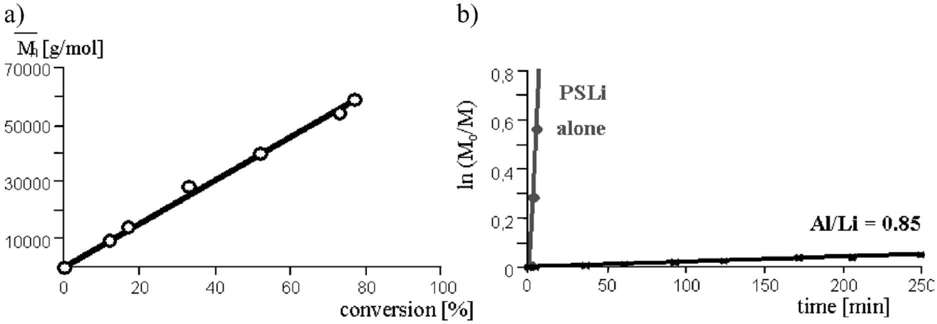


Figure 8.
(a) Average number molar masses Mn versus time and (b) k_{app} versus time of the styrene polymerization initiated by i-Bu_3Al/s-BuLi = 0.85, cyclohexane, 50 °C.

experimental molar masses versus time plot indicates that there is also no transfer, i.e. the polymerization exhibits a living character over the entire range studied. The anionic polymerization may even be conducted in a controlled manner at elevated temperatures, e. g. in polystyrene melts, namely under similar conditions as the free radical process.

U.V. spectrometry, kinetic studies and viscosimetric measurements suggest the presence of various types of mixed complexes of different stoichiometries [4]. Ab initio calculations are also in agreement with the formation of mixed complexes (Figure 9), the complex stoichiometry depending on the Al/Li ratio. At low ratio, a 2:1 complex, in which one s-BuLi is directly linked to the aluminum derivative, is firstly formed with a stabilization energy of about −1100 kJ/mol. Then, at higher ratio, a 1:1 complex is finally formed. The lower stabilization energy (−160 kJ/mol), when going from the 2:1 to the 1:1 complex, suggest that both species are present as long as the Al/Li ratio does not reach 1.

The monomer insertion could proceed according to two distinct routes: either a direct insertion into the 2:1 aluminate complex or an indirect insertion, involving the chain growth via dissociated lithium species, the complex would be considered as dormant in equilibrium with a very low proportion of free lithium species. Many

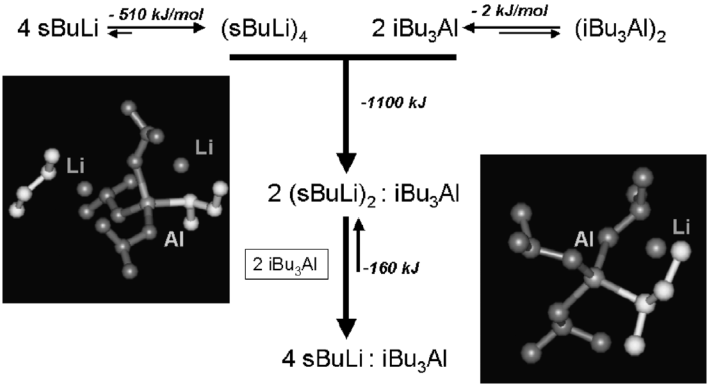


Figure 9.
Ab initio calculation concerning the formation of s-BuLi and i-Bu_3Al homocomplexes and heterocomplexes. Computational Methods - Density Functional Calculations: Karlsruhe TURBOMOLE quantum chemistry package, geometry optimization with the TURBOMOLE split valence (SV) (7s3p)/[3s2p] basis sets.

arguments, such as stability of active species at very high temperature and reactivity in copolymerization (see later), supports the direct participation of aluminate complexes in the polymerization.

The reactivity extinction, observed at a Al/Li ratio equal to one, is consistent with the inactivity of the 1:1 complex which is quantitatively formed at this ratio, whereas at ratio Al/Li lower than one, the strong decrease in polymerization rate could be explained by the presence of a 1:2 (Al:Li) complex of low activity. Therefore both active and ‘‘dormant’’ chains coexist at Al/Li ratio ranging from 0 to 1. Fast dynamic equilibrium between the 1:2 and 1:1 complexes, through exchange reactions, results in the formation of a constant number of polystyrene chains, even at ratio close to one.

Data reported, so far, for retarded styrene polymerization with trialkylaluminum/alkyllithium systems were consistent with the unique contribution of RLi species and the absence of any input of the trialkylaluminum derivatives in the formation of additional PS chains. The MALDI-Tof analysis of a PS initiated with n-HexLi/i-Bu_3Al gives only one PS population with an hexyl group, proving that the i-Bu_3Al does not act as initiator or transfer agent but only as retarder (Figure 10a). In contrast, with the i-Bu_2AlH system, experimental molar masses are about half those theoretically calculated from the PSLi seed concentration, suggesting the occurrence of a second chain generation process. In the presence of PSLi initiated from s-BuLi, 2 populations can be effectively observed by Maldi-Tof, one with a H terminus and the second one with a Bu one (Figure 10b). This indicates, that in contrast to Al–R bonds, the Al–H bond can be an efficient chain carrier as long as the reactivity remains sufficiently low ($Al/Li > 0.8$) to enable a fast exchange between each species.

These aluminate systems exhibit also an interesting behavior towards butadiene polymerization and copolymerization. Whereas the microstructure of a polybutadiene initiated from Al/Li systems is very close to that obtained in hydrocarbon with a conventional Li-initiated polymerization, i.e. 10–12% 1,2 vinyl units, a drastic change in the copolymerization parameter was noticed. This allows, for the first time, to get simultaneously random S/B copolymers while maintaining a very low content of 1,2 units.

Finally, the effect of R_3Al on the active species stability is also of great worth. At 100 °C, PSLi species undergo a fast degradation corresponding to the leaving of a LiH to form an unsaturated end-chain. Attack of this unsaturated end by another PSLi yields an isomerized lithium species considered as inactive (Figure 11). Under the same conditions, the presence of i-Bu_3Al leads to a strong increase of the polymer-end stability and a suppression of the isomerization process. For instance, the half-life time of the active species is increased by a hundredfold at a Al/Li ratio equal to 0.85. The use of aluminum additives containing one Al–O bond leads to a further increase of the stability.

It has been already mentioned that Li species alone lead, in bulk, to a very fast and uncontrolled reaction with temperature raising 300–400 °C in the reactor. In such conditions, transfer reactions reduce strongly molar masses whereas termination processes result in a polymer coloration. With the aluminate system in the same conditions, the half-time reaction is of several minutes instead of few seconds without aluminum additive. As a result, the polymerization heat can be efficiently removed and clear transparent polystyrene of high molar mass can be prepared allowing the retarded anionic polymerization to be run in conventional radical plants.

However, the HIPS process has a strong influence on the product morphology. The radical process involves polystyrene grafting on the polybutadiene chains. The excess of PS and the stirring in the vessels lead to the formation of polybutadiene particles with a diameter of 1.5 to 3 μm in the polystyrene matrix (Figure 12a). The rubber particles are filled with polystyrene

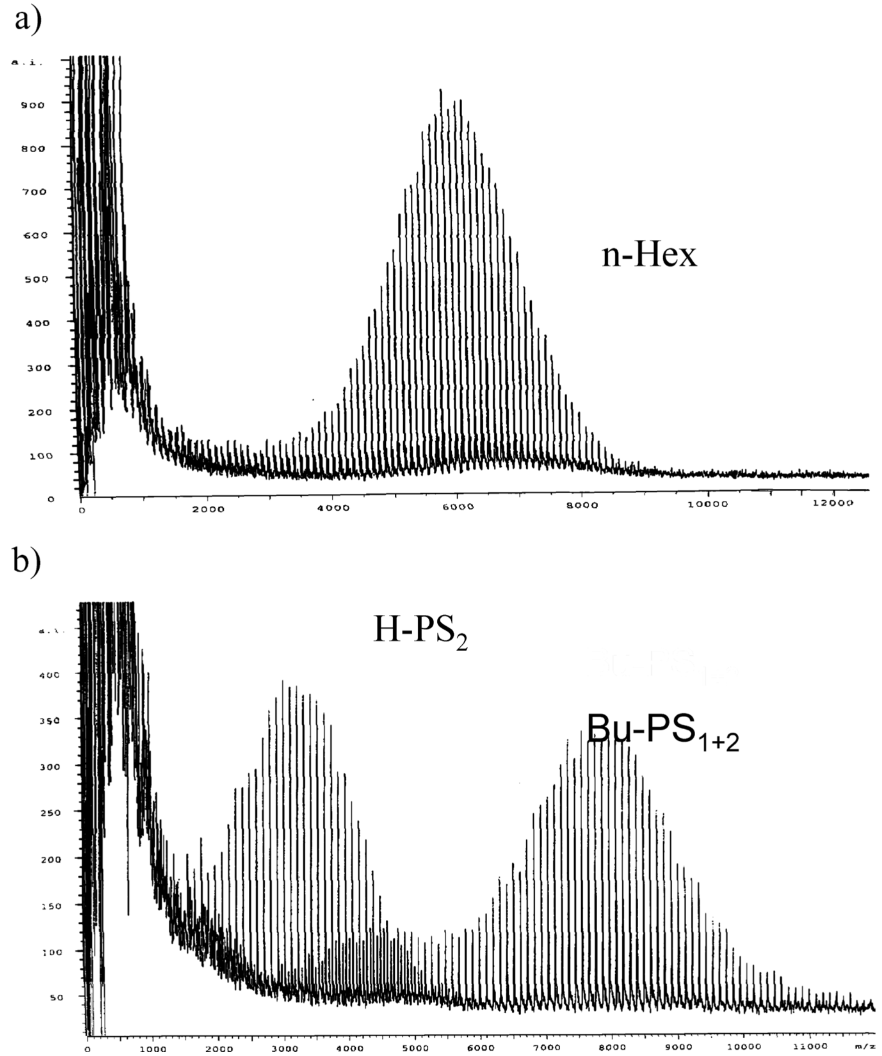


Figure 10.
MALDI-MS (Matrix Assisted Laser Desorption Ionization Mass Spectrometry) analyses; (a) styrene polymerization initiated by i-Bu_3Al/n-HexLi, (b) styrene polymerization initiated by i-Bu_2AlH/PS_1Li, R_3Al / RLi = 0.85, cyclohexane, 50 °C. The MALDI-MS measurements were performed on a BIFLEX III instrument (Bruker Daltonik GmBH, Bremen). The polymers and the matrix Dithranol (1,8,9 Trihydroxyanthracen) were dissolved in THF at concentrations of 10 g/L and 20 g/L respectively. Then the Polymer and matrix solutions were mixed in a 1:1 ratio (i.e. 20 μL each). As cationizing agent, 5 Vol. % (2 μL) of AgTFA (silver trifluoroacetic acid 0.02 molar in THF) is added and this mixture then spotted on the sample holder.

inclusions, which allow an increase in the rubber efficiency. The surface of this material after cold break appears homogeneous, indicating a good cohesion between the two phases. In the anionic process, grafting of the polybutadiene does not occur and the PS/PB phases cannot be connected with copolymers. As a result, the morphology is different: 2 phases are present without inclusions and the rubber cannot act effectively as an impact modifier (Figure 12b).

The retarded anionic polymerization of styrene proceeds in the same manner and polystyrene cannot be grafted on the rubber chains. Hence, polybutadiene used for

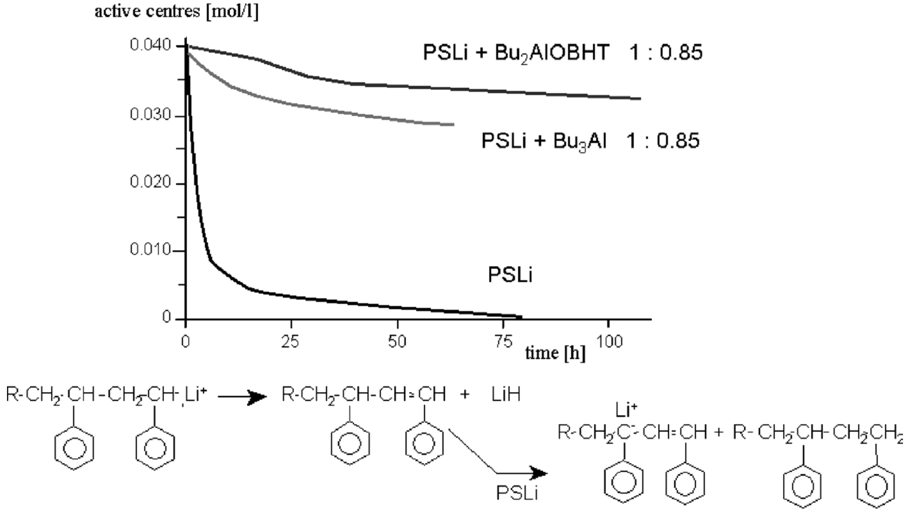


Figure 11.

Active centre concentration [Li] versus time, cyclohexane, 100 °C. Concentration of Li species has been determined via UV spectroscopy. The absorption spectra of the polystyryllithium/aluminum derivatives solutions were recorded on a UV-Vis spectrometer Varian-Cary 3E using a quartz cell (0,01 cm path-length) attached to the glass reactor; $\varepsilon_{PSLi} = 13000$ mol · dm^3 · cm^{-1} at 326 nm, $\varepsilon_{styrene} = 450$ mol · dm^3 · cm^{-1} at 290 nm.

radical HIPS is replaced by a styrene-butadiene block copolymer to allow cohesion between the polystyrene and the polybutadiene phases. This rubber is made in-house in a batch process similar to Styrolux®: a conventional anionic polymerization is used in solution initiated with BuLi [2].

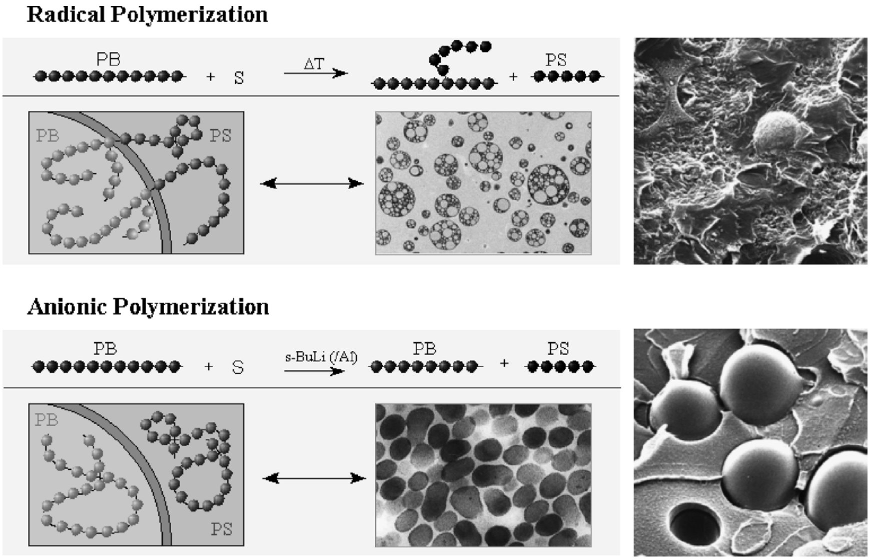


Figure 12.

Rubber morphology from a standard homopolybutadiene after radical polymerization (a) and anionic polymerization (b), including electronic micrographs stained with OsO_4; white domains: polystyrene (PS), dark domains: polybutadiene (PB).

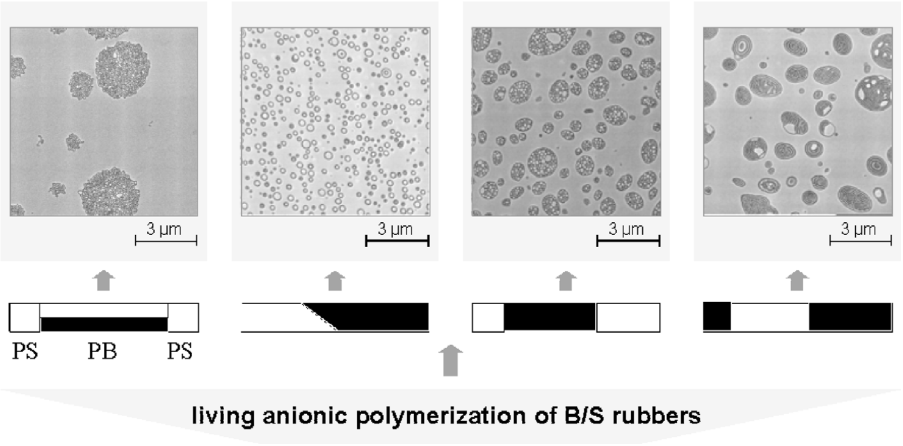


Figure 13.
Rubber morphology obtained after A-HIPS process according to the nature of the rubber; electronic microscopy after staining with OsO_4; white domains: polystyrene (PS), dark domains: polybutadiene (PB).

According to the nature of the rubber, various morphologies are obtained (Figure 13), as for instance: labyrinth or core shell rubber particles, the conventional salami structure with an asymmetrical SBS rubber or the onion morphology.

Since 1995 a strong effort has been directed at the development of new systems to adapt the anionic polymerization process to the commodity polystyrene market. Within the R.A.P. concept, dialkylmagnesium/alkyllithium combinations (Figure 14) were the first systems able to ensure the anionic styrene polymerization at temperatures around 100 °C in concentrated media under potentially useable industrial conditions. The lowering of the initiator cost that has been steadily stressed and the reactivity control up to about 150 °C led us to a second generation of R.A.P. initiating systems associating alkyllithium to alkylaluminum compounds. We have recently proven that the simple combination of metal hydride with trialkylaluminum, two inactive components by their own in styrene polymerization, allows the anionic polymerization of styrene [4]. These new low cost anionic initiators (BuLi-free), based on the combination of trialkylaluminum with alkali metal hydride, in particular sodium hydride, allow reactivity control over a broad temperature range at monomer concentrations up to bulk. The reduction of the initiator costs by a factor 10 with these third generation systems allows industrial anionic styrene polymerization with production costs

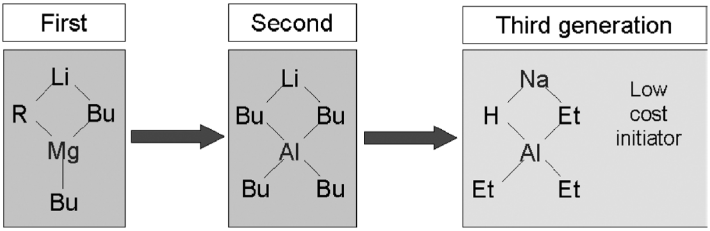


Figure 14.
Representation of various retarded initiator systems used in anionic polymerization of styrene; first generation (1995): n,s-Bu_2Mg/s-BuLi, second generation (2000): i-Bu_3Al/s-BuLi, third generation (2003): Et_3Al/NaH.

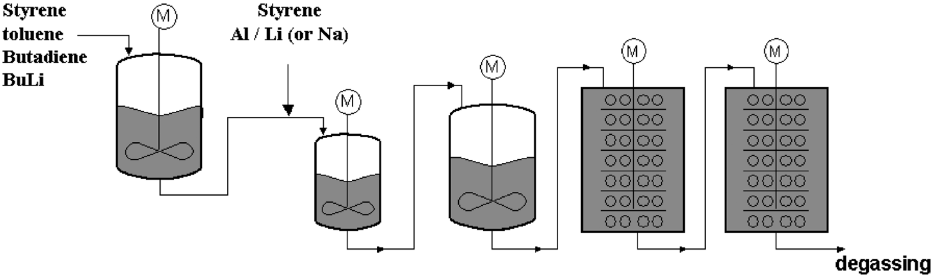


Figure 15.
A-HIPS process: vessel-vessel-tower-tower reactor configuration.

close to the radical process and should open the way to a rapid commercialization of the resulting polymers.

We are currently investigating a ''drop-in'' process to implement this new technology into an existing plant set up (Figure 15). This process can be depicted in two parts: a conventional batch anionic polymerization of a SBS rubber in toluene and a continuous HIPS synthesis after styrene and retarder addition. From a standard SBS rubber, a retarder/initiator system is added and the styrene polymerization is carried out under the same conditions and with the same plant configuration as for the R-HIPS process (see Figure 2). Upscaling experiments have confirmed the possibility to run A-HIPS with comparable or even better mechanics than the conventional product by formation of conventional salami morphology. Using the new retardation agent the product properties were within the range of a typical radical HIPS specification over a period of several weeks. Additionally, as anticipated, a much better organoleptic quality is reached. This product contains less than 5 ppm styrene and ethylbenzene and less than 200 ppm

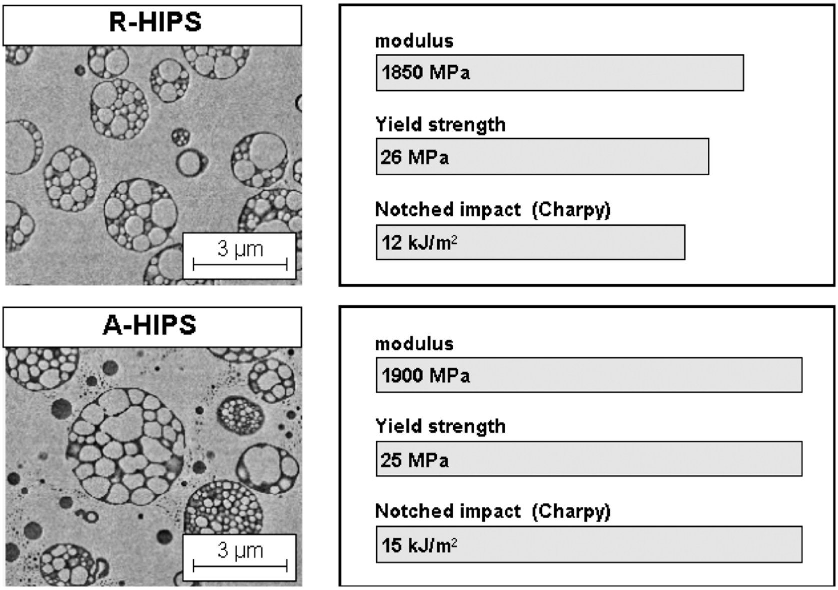


Figure 16.
Rubber morphology obtained after R-/A-HIPS process and resulting mechanics; electronic microscopy after staining with OsO_4; white domains: polystyrene (PS), dark domains: polybutadiene (PB).

polystyrene oligomers, compared to significant higher values for the radically manufactured HIPS.

During first customer test of HIPS packaging product, such as a standard yogurt beaker, A-HIPS was evaluated as identical or similar to R-HIPS concerning mechanical properties and thermoforming behavior (Figure 16). The lower amount of residual styrene gives additionally a better organoleptic property. Last but not least, a significant cost reduction has also been reached, due to the higher space time yield, the possibility to increase the butadiene content without negative impact on properties by rubber architecture tuning and the possibility to add cheap filler via in situ anionic polymerization or by blending. With these optimizations A-HIPS is even cheaper than R-HIPS.

Conclusion

BASF has succeeded in operating a continuous retarded anionic HIPS polymerization on a pilot plant scale (200 t/year) and has developed an A-HIPS injection molding and extrusion grade with a property profile comparable to its radical counterpart however free of residual styrene and with a much lower content of styrene oligomers. Thanks to the internally developed initiator and reactor design technology, specific investment for a grass route plant is similar to the radical process but includes in situ rubber production. This new technology leads to an interesting reduction of variable costs. The implementation of this process into an existing radical plant set up (drop in solution) without the necessity of major investments is a further option for a rapid commercial production of A-HIPS. The gate for further innovative products provided by retarded anionic polymerization is opened.

[1] H. Gausepohl, V. Warzelhan, *Angew. Makromol. Chem.* **244**, 17 (1997).
[2] H. Gausepohl, R. Gellert, Eds., "Polystyrol", *Kunststoff Handbuch* **4**, Carl Hanser, Munich, 1996.
[3] W. Schlenk, J. Appenroth, A. Michael, A. Thal, *Chem. Ber.***47**, 473 (1914).
[4] a) P. Desbois, M. Fontanille, A. Deffieux, V. Warzelhan, S. Lätsch, C. Schade, *Makromol. Chem. Phys.* **1999**, *200*, 621. b) A. Deffieux, P. Desbois, M. Fontanille, V. Warzelhan, S. Lätsch, C. Schade in Puskas, J. E. et al. (eds), *Ionic Polymerization and Related Processes*, Kluwer Academic Publishers, 1999, 223–227. c) S. Ménoret, S. Carlotti, M. Fontanille, A. Deffieux, P. Desbois, C. Schade, W. Schrepp, V. Warzelhan, *Macromol. Chem. Phys.* **2001**, *202*, 3219. d) P. Desbois, M. Fontanille, A. Deffieux, V. Warzelhan, C. Schade, *Macromol. Symp.* **2000**, *157*, 151. e) A. Deffieux, S. Ménoret, S. Carlotti, M. Fontanille, P. Desbois, C. Schade, *Macromol. Chem. Phys.* **2002**, *203*, 862. f) S. Ménoret, M. Fontanille, A. Deffieux, P. Desbois, *Macromolecules*, **2003**, *36*, 5988. g) S. Carlotti, S. Ménoret, A. Barabanova, P. Desbois, A. Deffieux, *Macromol. Chem. Phys.* **2004**, 205 (5), 656. h) S. Carlotti, S. Ménoret, P. Desbois, A. Deffieux, L. Shcheglova, A. Barabanova, J-M. Maréchal, *Macromol. Symp.* **2004**, *215*, 17. i) S. Carlotti, S. Ménoret, A. Barabanova, P. Desbois, A. Deffieux, *Polymer* **2005**, 46(18), 6836. j) WO 98/07765. k) DE 19731419. l) US 6410654. m) DE 10218161.