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QUO VADIS IONIC POLYMERIZATIONS

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Abstract: This presentation concerns subjective comments in respect to the status and foreseeable future of ionic polymerizations, i.e., cationic-, anionic-, and ionic ring opening polymerizations.

INTRODUCTION

The assignment I got from the organizing chairmen sounded deceptively simple: For the first lecture the organizers suggested an "ecumenical" presentation, that is a presentation which addresses all the "denominations" in the ionic polymerization community. These marching orders make perfect sense: At the start of such a large international gathering of distinguished investigators representing a very wide spectrum of interests in ionic polymerization, an effort should be made to start with an analysis of the status of the field and then to ask: Where are we going? Where should we be heading? Hence the title: Quo Vadis Ionic Polymerization?

From my personal point of view this assignment was a difficult one. My presentations usually concern specific research findings and occasionally an overview of recent advances in my area of expertise, that is in cationic polymerizations, but certainly not the surveying and analysis of such an enormously large area as ionic polymerizations in general. Evidently the organizers believed that after having spent over three decades in ionic polymerizations research, I will have the guts to say something about the status of our field, and the gumption to stick out my neck by glimpsing into the foreseeable future.

After considerable agonizing I have accepted the challenge, however, I want to start with a disclaimer: This presentation will largely consist of personal opinions reached after a lot of cogitation and discussions with friends and colleagues, and the views expressed in this lecture are only those of the speaker and in no way reflect the views of the "management".

DEFFNITION AND SCOPE

Obviously, a presentation such as this must begin by defining the subject: Ionic polymerizations are chain growth (or addition) polymerizations in which propagation involves electrically charged

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i.e., ionic, species; specifically, cationic and anionic polymerizations, and ring opening polymerizations which proceed by ionic active centers. ROPs proceeding by covalent species are beyond the scope of this definition.

Polymerizations mediated by organometallic compounds or metallocenes, as well as coordination/insertion polymerizations are also not covered by this definition. My assignment would have been a lot easier and much more upbeat had I been able to include these areas in my presentation.

ACADEMIA ↔ INDUSTRY AND THE PRODUCT LIFE CYCLE

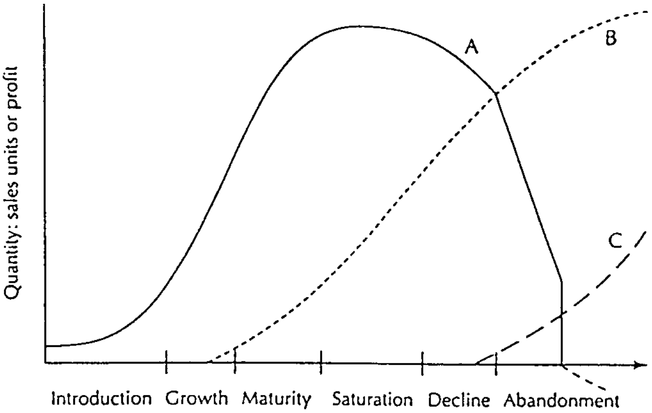
Let me start by making a few remarks relative to the current academia/industry interphase. Without making value judgments, let me observe how strongly industrial thinking controls contemporary academic research. Ten and certainly 20 years ago the generation of new fundamental information was sufficient to attract funding from the large funding agencies or from research-oriented industrial corporations. In contrast, today, proposals are judged not only by their scientific content but also (indeed decisively) by their technological, societal, and environmental significance. The decisive impact of industrial/technological considerations is vividly illustrated by funding agencies often demanding documentation of support by “the industrial partner”. Whoever heard of the necessity of a supporting letter by the industrial partner some 10-20 years ago? These agencies have of course not invented these changes: they only reflect the unrelenting pressure exerted by the public and business on government.

The situation was quite different in the 50's and 60's when I started my independent research career. Then the emphasis was on *new* and not on *useful,* fundamental research was king, and the message in industrial laboratories was "create something new, we will then manage it and find a way to sell it". In retrospect and in light of current happenings, it is difficult to comprehend the naivit6 of industrial research management during those halicon days of fundamental research.

My main point is that in vain do we prepare today new polymer architectures, if they are not useful and will not in some form impact the market place, they will die unripe and will be gathering dust in the what I call "a cookie and a handshake" research literature. I hope most polymer synthesis researchers will accept of this contemporary truth.

Since we are considering the influence of business on polymer chemical research, let me remind you of the concept of the Product Life Cycle (PLC). Very briefly, according to the PLC, one of the very few generally accepted “laws” of business, every product or service that exist in the market place undergoes 6 distinct phases with well defined characteristics: 1) Introduction, 2) growth, 3) maturity, 4) saturation, 5) decline, and 6) abandonment (see Figure 1). The aim of business is to perpetuate the saturation phase, which it strives to accomplish by bringing out a stream of products one after the other, so that the decline phase of a product A is offset by the maturity phase of the next product B (see Figure 1). In this manner the sales volume and/or profits will not decline and the enterprise will survive.

Figure 1. The product life cycle: A, B and C are generations of products.



The PLC has served me well not long ago analyzing the "Past-Present-Future of Cationic Polymerizations" (1). I found that the PLC concept is also valid to my business, the business of research, and I found it quite useful helping me with project selection and assessment in cationic polymerizations. With the help of the PLC I was able to evaluate the "past", to pinpoint where the "present" started, and to formulate projects for the "future". I am taking this opportunity to update my 1995 views on cationic polymerization, and to extend my analysis to anionic and ring opening polymerizations, also in terms of the PLC.

QUO VADIS IONIC POLYMERIZATION

1. Cationic Polymerization

The last "quantum jump" in cationic polymerization research occurred in the mid 80's with the discovery of living polymerization of isobutylene (IB) and alkyl vinyl ethers (for a chronology and analysis of these discoveries see references 2 and 3). Living cationic polymerizations were held unattainable not much before the publications of these pioneering investigations. These discoveries immediately spawned research and development both in academic and industrial laboratories.

Mechanistic studies are still ongoing and focus on the definition of the active propagating species and elucidation of parameters which give rise to livingness of cationic systems.

To me it is of particular interest from the scientific-historical point of view that the quasiliving equilibrium concept of termination (i.e., the very rapid equilibrium that exists between inactive-dormant and active-propagating species) in cationic polymerizations is also one of the key requirements of recently discovered living free radical polymerizations. The consequences of the rapid quasiliving equilibrium in cationic systems was analyzed and developed in quantitative terms much before the latter discovery (4).

For obvious reasons it is difficult to obtain meaningful information in regard to current industrial research activity on living cationic polymerizations. Interest in the exploitation of living polymerization of IB by petrochemical-oriented companies can be perceived by their patent activity. Polyisobutylene (PIB) provides an excellent combination of mechanical-chemical properties for very low cost (IB is one of the cheapest hydrocarbon monomers) and the living cationic polymerization and copolymerization of IB now enables the precision syntheses, in terms of controlled molecular weight and molecular weight distribution, of PIB-based elastomers.

Specifically, I am looking forward toward new developments in two PIB-based applications: 1. Sequential, i.e., block and star polymers and 2. Terminally-functional PIBS. PIB-based block and star polymers present an uncommonly broad spectrum of possibilities. Diblock polymers and/or random grafts of IB and styrenic polymers maybe of use for compatibilization or emulsification of PIB or butyl rubber with polystyrene (PSt) and styrenic polymers; these two groups of inexpensive widely-used polymers are hopelessly immiscible and give useless mixtures. PSt/PIB blends compatibilized by PIB-*b*-PSt diblocks may lead to new grades of impact polystyrenes for outdoor applications (PIB is a saturated rubber with outstanding environmental resistance, whereas the unsaturated polymers of conjugated diene monomers currently used for impact enhancement must be stabilized). Perhaps even more intriguing are possibilities offered by PSt-*b*-PIB-*b*-PSt triblocks which exhibit excellent thermoplastic elastomer characteristics. The mechanical properties of these TPE triblocks match those of commercially successful Kratons® obtained by living anionic polymerizations (5). Recently multi-arm block-stars, $(\text{PSt-}b\text{-PIB-})_n$-core, which combine the expected excellent mechanical properties of the corresponding triblocks with processing advantages (low melt viscosities), have been prepared. Such stars have also promise as rheology control agents in lubricating oils.

In regard to new developments in end-functionalized PIB, I recently learned that Kanegafuchi in Japan announced the commercialization of a new allyl-telechelic PIB: $CH_2{=}CH{-}CH_2$~~~PIB~~~$CH_2{-}CH{=}CH_2$, "Epion", made by the living polymerization of IB.

One of the intended applications is in sealants.

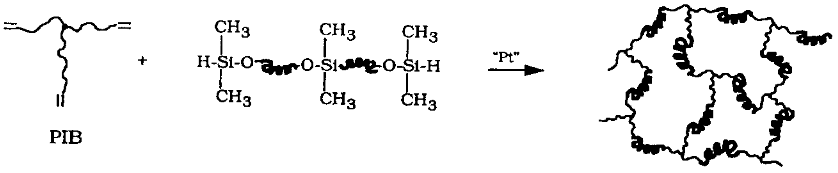
Another area in which I would expect advances is the exploration of environmentally friendly "green" solvents or conditions in ionic polymerizations in general and cationic polymerization in particular. The first steps have already been undertaken and we know that CO_2, both supercritical or liquid CO_2, is a good diluent for cationic polymerizations and that the molecular weight of PIB prepared in supercritical CO_2 is surprisingly high (6). CO_2 is an excellent solvent for a variety of Friedel-Crafts acids (e.g., BCl_3, $TiCl_4$, SnCl,) and of hydrocarbon polymers of less than ~2500 g/mol. Since CO_2 is not a solvent for high molecular weight polymers (except for fluorocarbon and silicone polymers), further advances will necessarily concern heterophase or dispersion polymerizations which will necessitate the assembly of novel dispersing agents. These dispersing agents will most likely be combinations of fluorocarbons or siloxane moieties (CO_2-philic) with polyhydrocarbons (CO_2-phobic).

Another area whose time has come is living cationic isomerization polymerizations. The first steps have already been undertaken with β-pinene (7).

I would not be surprised to witness a renaissance of research in non-living cationic polymerizations proceeding by highly reactive counterion-unencumbered ("free"?) carbenium ions. The great advantage of these systems is very high molecular weights, for example with PIB and IB copolymers, produced in lighteningly fast reactions. Similar polymerizations by conventional Friedel-Crafts acids (e.g., BF_3, $AlCl_3$) which involve initiation by acids arising from protic impurities and coordinating counteranions ($BF_3OH^{\ominus}$, $AlCl_3OH^{\ominus}$ (8)), are still among the most important cationic polymerizations and are commercially practiced on a very large scale all around the globe (9). Among the great disadvantages of these "classical" processes is the need for very large quantities of chlorinated chemicals (e.g., methyl chloride diluent, aluminum chloride), and the use of cryogenic temperatures (close to -100°C). One possibility of eliminating the noxious chemicals may be by γ-ray initiation in bulk in tubular reactors. That y-ray initiated bulk polymerization of IB rapidly yields very high molecular weight products with acceptable molecular weight distributions (Mw/Mn = ~2.0) has been demonstrated (10). Regrettably, there is a stigma associated with high energy radiations which may delay developments. In line with this chain of thoughts, it would be intriguing to find cationic polymerizations initiated by chemical means but proceeding by unencumbered carbenium ions similar to those existing in γ-ray initiated systems. The use of acids or salts having non-coordinating counteranions, e.g., $B\text{-}(\text{-}C_6F_5)_4^{\ominus}$ (8), may lead to polymerizations induced by chemical initiating systems in conventional reactors exhibiting the desirable characteristics of γ-ray initiated polymerizations, i.e., highest molecular weights, high rates, narrow molecular weight distributions, in the absence of massive amounts of chlorinated ingredients. This objective may be attainable and IB polymerization to high molecular weight reasonably narrow molecular weight distribution polymers have been prepared by novel chemical initiating systems with non-coordinating anions (11). Recently we have obtained highest molecular weight IB homopolymers and copolymers, Mn > 100,000 g/mol in the 0° to -20°C range, by chemical initiation. To-date such high molecular weight PIBs could be prepared only by γ-ray initiated polymerizations (10).

And since we have touched upon irradiation-induced polymerizations, let me mention the status of photocationic polymerizations. The seminal discoveries were done about two decades ago when it CD was found that certain iodonium and sulfonium cations neutralized by stable anions, such as $BF_4^{\ominus}$, $SbCl_6^{\ominus}$, when irradiated by UV light, mediate rapid proton-initiated polymerizations (12). Since then these findings became the foundations of new industries, specifically new coating and printing (lithography) technologies. The main advantage of these processes is that they are rapid and environmentally friendly, i.e., they are practiced by irradiating bulk formulations in the absence of volatile solvents. While the latest industrial developments are cloaked in secrecy, progress can be sensed by following the patent literature. The ongoing research by a large number of investigators active in this field make me optimistic in regard to the future of photocationic polymerizations.

In 1995 I expected further advances in the exploration of combinations of hydrocarbon and silicone rubbers with the main objective of enhancing the poor mechanical properties of the latters. Recent results indicate that this objective can indeed be obtained by means of novel bicomponent networks prepared by hydrosilating three arm star allyl-telechelic PIBs with HSi-terminated linear polydimethyl siloxanes (13):



Surprisingly, sheets of these networks were optically clear which indicates intimate phase mixing between the polysiloxane and PIB sequences, two polymers which are completely immiscible with each other. Other synergistic developments at the interphase of polyhydrocarbon and silicone chemistries are the recent emergence of multi-arm stars, for possible applications as additives in paints or lubricating oils, consisting of PIB arms held together by a simple (14) or complex (15) cyclosiloxane core.

The recognition that living free radical polymerizations are readily initiated by benzylic or tertiary chlorides, i.e., by species that form by living cationic polymerizations (2), should lead to new sequential copolymers by a combination of these two powerful techniques. Indeed, the first breakthroughs have already been described with the preparation of poly(styrene-*b*-methyl methacrylate) and similar block polymers (16).

And finally, Quo Vadis alkyl vinyl ethers? The discovery and seminal exploration of living polymerization of this group of monomers was a marvelous achievement of Kyoto University investigators (for reviews and summaries see Refs. 2 and 3) and has opened avenues for the synthesis of many novel microarchitectures. The challenge now shifts to development, to find a breakthrough application for this group of materials. In view of the relatively high cost of these monomers (relative to hydrocarbon monomers) the future of these polymers will be in well-defined specialties, e.g., new biomaterials, electronic applications. The exploration of novel PIB-based biomaterials e.g., bio- and hemocompatible amphiphilic membranes, delayed drug delivery reservoirs, improved bone cements, immunoisolation devices, is in full swing (17).

In sum, living cationic polymerization, discovered only a short decade ago, has not yet fulfilled its promise and did not mature into commercial products (except Epion). As suggested by the history of living anionic polymerizations, however, there is still a lot to be learned and exploited in this rapidly emerging field.

2. Anionic Polymerization

The modem era of anionic polymerization starts with Szwarc's work in the mid 1950's which culminated in the discovery, recognition and systematic development of living polymerizations in general. There were others who much earlier had living anionic polymerization in their hands but failed to recognize its true significance and didn't capitalize upon it. (This reminds me of the Vikings who have "discovered" America, but returned home to Scandinavia without doing too much about their epochal discovery.) After the principal facts of living anionic polymerizations have been laid out in the scientific literature (interestingly Szwarc never protected his discoveries by patents), his breakthrough was exploited by industrial researchers (18). These workers and their organizations created the foundations of several highly successful industrial processes such as styrenic TPE'S, new general purpose rubbers including solution SBR, etc. (18). Research aiming at the further scientific and technological exploitation of living anionic polymerization is still in progress, both in academia and industrial laboratories, and bespeaks the importance of the original breakthrough. Indeed, the significance of the original discovery far exceeds anionic polymerizations; it also spawned similar efforts in other areas, notably in cationic polymerization (see above), and organometal-induced coordination/insertion polymerizations.

In sum, the importance of anionic polymerizations, or more specifically, alkyllithium-mediated living anionic polymerizations, in today's research and commercial activity is unquestioned. In the PLC sense, the field is in the maturity phase, and I expect many years of healthy activity both in research and development laboratories. As to where the future lies, I see more of the same: steady growth toward new microarchitectures, however, with increased sensitivity of linking knowledge with end-use. While the tallest peaks have already been climbed, there remain plenty of worthwhile hills for the future: terminally-functional prepolymers and telechelics for industry, further research with additives (e.g., LiCl), stereoregulation, controlled acrylate polymerizations, continued exploration of the polymerization of polar monomers, diblocks of dissimilar sequences, i.e., hydrophobic-*b*-hydrophilic and crystalline-*b*-amorphous combinations.

3. Ring-Opening Polymerizations

Sustained high level of activity in ionic ring-opening polymerizations is apparent both in academic and industrial research arenas. In regard to the latter, let us be reminded at the growth in the many large industries based on ROPS, i.e., the polymers and copolymers of ethylene- and propylene oxide, tetrahydrofuran, trioxane, ethyleneimine, ε-caprolactone, caprolactam, cyclic siloxanes. After having surveyed some of the current literature, and listening to investigators active in ROP, I have come to the conclusion that the most watched promising current development in this field is the polymerization of macrocyclics.

In conventional ROPS, e.g., in cationic tetrahydrofuran or anionic lactone or siloxane polymerizations, the preferred route to linear polymers is from small-ring precursors, and the formation of medium-sized cyclic oligomers (dimers, trimers) is considered undesirable. In contrast, according to the new ROP technique, mixtures of cyclic oligomers ("cyclomers") are the preferred starting materials (19). The driving force for this new technology is the use of low viscosity precursors, the possibility of preparing higher than conventional molecular weight polymers (by nonstep growth kinetics), the possibility of reactive processing because of high rates with no or very little volume change and no volatiles, and the possibility of using matrices for composites by resin transfer molding. Development is carried out by GE and Ford researchers, specifically to prepare polycarbonate resins from mixtures of mainly trimers, tetramers and pentamers of cyclic polycarbonates; such mixtures are desirable starting materials because their melting temperature is much lower than those of pure products which leads to lower processing temperatures. Similarly, terephthaloyl dichloride plus 1,4-butanediol yielded cyclic dimers to octamers, mixtures of which could be readily polymerized to high molecular weight (Mw > 60,000) products at -200°C in 15 min. Further developments concern research at Dow on polyethersulfones $-(-pC_6H_4-SO_2-pC_6H_4-O-)_n-$ (21), prepared from the corresponding cyclic oligomers, and Kevlar-like polyamides by DuPont chemists $-(\text{-N.sBU-pC}_6\text{H}_4\text{-N.sBU-CO-C}_6\text{H}_4\text{-CO-})_n-$ (22).

While progress is rapid and truly remarkable advances have been made, many problems remain which have to be overcome before commercialization becomes a reality. Among the more apparent obstacles are: The melting temperatures of the starting materials are often too high (cyclooligomer distribution is too narrow) to yield cost advantages over conventional ROP; The efficiency of cyclization chemistry is poor leading to low yields; Linear oligomer impurities may be present which then function as potential chain transfer agents.

My last comment in regard to ROPS: One of the fundamental shortcomings of ROP is that because the reactive site in the heterocyclic ring monomer(s) enters the polymer chain virtually unchanged, secondary reactions involving the new chain inevitably occur and lead to ill-defined by products at the expense of the target polymer. (In one unique instance, with N-tert-butylaziridine, this problem could be eliminated (23)). It would be desirable to find a general concept to overcome this "built-in" difficulty. A conceptually similar problem has been overcome in numerous ROMP systems where, although the reactive site (unsaturation) in the monomer was transferred into the new chain, nonetheless, livingness could be achieved (24).

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