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Application of a Direct Cooling Method in the Cationic Polymerization of Isobutylene

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patible with relatively high transfer constants and which are limited at the present time to low-mol.wt. polymers, which I prefer to call "apparently living polymers" even if in the future they may pass into the other category.

Living radical polymerization has long been expected to be still less possible in view of the strong tendency of radicals to react together to give rapid termination reactions. However, some attempts at block copolymerization have been successful with usual polymeric radicals trapped into crosslinked or other very viscous media. But the most interesting idea has been that of using systems with reversible termination. If a nonsymmetrical initiator $R-R'$ is split into two radicals $R\cdot$ and $R'\cdot$, and if the monomer is initiated only by $R\cdot$, the growing polymer chains $R-M_n\cdot$ may react either with themselves (leading to termination) or with $R'\cdot$, giving $R-M_n-R'$, which may also be capable of initiation and further growth. If the crosstermination giving $R-M_n-R'$ is favored compared to the symmetrical ones, a system more or less near a living one might be obtained. Up to now, there were only a few examples of initiators and monomers that seemed to behave in that way (particularly with styrene, methylmethacrylate, and acrylates), but secondary reactions occur and no perfect system has been described yet. However, if $R'\cdot$ groups that do not recombine may be used, as has been proposed recently, it might be possible to obtain again systems still nearer to living polymers.

APPLICATION OF A DIRECT COOLING METHOD IN THE CATIONIC POLYMERIZATION OF ISOBUTYLENE

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Inspired by the Leidenfrost phenomenon, a direct-cooled, general-purpose, low-temperature reactor has been developed and its applicability for polymerization was demonstrated. The Leidenfrost reactor is effi-

ciently cooled by introducing relatively inexpensive liquid N_2 (LN_2) directly into the bulk of polymerization charges; the rapid evaporation of the coolant chills the system. The gaseous N_2 generated provides an inert gas blanket that protects moisture- and/or air sensitive charges. The installation of expensive cooling jackets or coils is superfluous and stirring is optional. The virtually complete recovery of cooling energy is possible. In the Leidenfrost reactor, the LN_2 heat sink is virtually in contact with the heat source so that the path of heat transfer is practically nil.

Reactor fouling is eliminated, which is of particular interest in butyl rubber manufacture. Constant temperature control is readily accomplished by regulating the input rate of the coolant, and undesirable temperature jumps are suppressed. Continuous operation is possible. The operation of the Leidenfrost reactor is illustrated by the polymerization of isobutylene at -60°C .

INTRODUCTION

Cooling, particularly to cryogenic temperatures, is expensive and the cost of cooling energy can only rise in the future. Large- or pilot-scale cooling of chemical reactors is usually effected by means of external or internal cooling jackets or coils containing a circulating coolant. In laboratory practice, reactors are conventionally externally cooled by immersion in a cooling bath containing the heat sink. Rapid stirring is mandatory in all these instances. Inherent major disadvantages of these types of conventional refrigeration are the high cost of refrigeration equipment (e.g., compressors, cooling jackets, or coil systems, coolants, stirrers), the necessarily incomplete utilization of cooling energy input, and the tendency of reactor fouling (see below).

Cooling, particularly at cryogenic temperatures, of air- or moisture-sensitive exothermic reactions is further complicated by the need for inert atmospheres (nitrogen, argon) with a constant slight positive pressure to prevent backdiffusion. For example, Friedel-Crafts syntheses in general and cationic polymerizations in particular are typical reactions that require efficient, sometimes cryogenic cooling under an inert atmosphere. Thus an elaborate dry-box system had to be devised which is in constant use in our laboratories for carbocationic polymerization research that requires cryogenic cooling and exclusion of moisture.

In this presentation we describe the principle and application of a

new type of inexpensive polymerization reactor that operates at low temperatures (from -180°C to -10°C) by injecting liquid nitrogen directly into the reaction medium.

The instantaneous flash evaporation of liquid nitrogen provides a large number of small bubbles (Leidenfrost phenomenon, see below) and thus efficient turbulent agitation (eliminating the need for special cooling equipment, stirrers). Further, the cooling energy input may be virtually completely recovered by controlling the evaporation, and the gaseous nitrogen generated in this process provides a blanket of inert atmosphere. The operation of such a "Leidenfrost reactor" is detailed and its use for polymerization is illustrated.

THE PRINCIPLE: THE LEIDENFROST PHENOMENON

The memorable Leidenfrost phenomenon occurs when, for example, a drop of water falls on a hot plate or LN_2 is spilled on the floor: The liquid breaks up into numerous small droplets, which vigorously move about until they completely disappear by rapid evaporation. Evidently due to the large temperature difference between the droplet and the relatively hot surface, a small portion of the liquid instantly vaporizes upon contact and the droplet vigorously rolls around on a cushion of vapor until the liquid completely evaporates.

Similarly, when LN_2 is injected directly into the bulk of another liquid, the LN_2 instantaneously evaporates accompanied by vigorous bubbling; the heat of evaporation is provided by the liquid medium and the temperature of the medium decreases in proportion to the amount of LN_2 used. This principle has now been exploited for the design of an efficient, low-cost, multipurpose reactor for carrying out reactions at low temperatures under an inert atmosphere.

THE LEIDENFROST REACTOR AND ITS ADVANTAGES

To maximize the path length of the ascending coolant bubble, the reactor is preferentially cylindrical. It is desirable to lengthen the residence time of the LN_2 in the reactor so that the bubble can completely vaporize before it reaches the surface of the charge. Under these conditions the cooling energy of the LN_2 is most efficiently exploited. The rapid evaporation of the coolant, particularly when the temperature of

the charge is above $\sim -50^{\circ}\text{C}$, causes strong foaming and thus agitation of the charge.

Since the heat source is the environment, the installing of expensive cooling surfaces (jackets or coils) becomes unnecessary, and the desired temperature is maintained by controlling the input rate of the LN_2 .

A stream of LN_2 is led into the charge by means of a glass tube and is dispersed through a sparger, a hollow glass bulb with holes. The efficiency of cooling is largely insensitive to the dispersion grade as long as a steady stream of LN_2 is maintained. Too finely dispersed streams (e.g., by the use of porous glass frits) tend to cause freezing at the pores, thus clogging the inlets. The moment the LN_2 hits the charge [whose temperature is usually much higher than that of the boiling point of LN_2 (-196°C)], the stream literally explodes into thousands of small bubbles composed of a LN_2 core surrounded by a shell of gaseous N_2 .

The LN_2 droplet is insulated from the bulk of the charge so that freezing can be avoided. The formation of numerous bubbles decreases the average density of the charge which promotes agitation. Dissolution of N_2 in the charge is of little importance since N_2 may be considered an inert diluent.

The residence time of the LN_2 droplet in the reactor may be extended by stirring or by the use of taller reactors (i.e., by scaling up). On the laboratory scale (3–5 L), stirring is optional because of the strong boiling of LN_2 provides sufficient agitation. In tall cylindrical industrial or pilot-scale reactors (>12 L), stirring should increase the residence time of the ascending LN_2 droplets and thus cooling is rendered more efficient. Indeed, larger Leidenfrost reactors are in general more efficient than smaller units, in which the liquid N_2 may reach the surface of the charge.

A major benefit of the Leidenfrost reactor is the ease and high rate it is able to compensate for sudden large temperature jumps. The area of cooling surfaces in conventional reactors is necessarily limited, and faster cooling can be achieved only by increasing the circulation rate of the coolant in the cooling jackets or coils. In these installations the maintenance of constant low temperatures may not even be possible in case of excessively rapid massive heat buildups. In contrast, in the Leidenfrost reactor the area of cooling surfaces (number of LN_2 droplets) can be virtually instantaneously increased in response to rapid temperature jumps by increasing the rate of coolant input. Also, the LN_2 cooling "surface" is in virtual contact with the heat source so that the length of heat transfer is minimum. The flow rate of the coolant can be automati-

cally regulated by connecting the input valve to a temperature-sensing device.

Another great advantage of the Leidenfrost reactor is that reactor "fouling" cannot occur. Fouling is the gradual accumulation of solids (i.e., polymer) on the cooling surfaces during operation, which leads to gradual reduction of cooling efficiency and ultimately to costly reactor shutdown.

The cleaning of cooling surfaces is a cumbersome, time-consuming operation. Fouling is quite common, for example, in butyl rubber manufacture, where fouling necessitates the use of more than one (usually three) parallel reactors to ensure continuous operation: while one of the reactors is shut down for cleaning, the rest are in operation.

Finally, the vaporizing liquid N_2 also provides a blanket of inert gas, which, particularly in smaller-scale (pilot plant) operations, may be quite advantageous to protect moisture-sensitive charges.

The Leidenfrost reactor can be used in the continuous or semicontinuous mode. In the continuous operation all the reactants and the liquid N_2 are metered in simultaneously into the reactor and the effluent is collected by a suitable outlet system. In semicontinuous operation the product is allowed to accumulate in the reactor.

In summary, the directly cooled Leidenfrost reactor is superior to conventional externally cooled reactors in view of the following advantages:

1. Simplicity of design, inexpensive equipment, installation of cooling surfaces unnecessary.
2. Use of relatively inexpensive LN_2 coolant (by-product of oxygen production).
3. Complete recovery of cooling energy stored in LN_2 in the form of heat of vaporization is possible.
4. Vaporization of LN_2 yields environmentally unobjectionable, nonpolluting, nontoxic gaseous N_2 .
5. The gaseous N_2 generated provides an inert gas blanket and protects moisture- or air-sensitive reactions.
6. Ease of scale-up; larger units tend to operate more efficiently than smaller units.
7. Ease of constant temperature control; massive temperature jumps can be eliminated by automatically increasing coolant input.
8. Can be readily converted to continuous operations.
9. Eliminates fouling problems.

10. Stirring optional, may be useful in large (> 100 L) reactors; boiling liquid N₂ provides agitation and a reduction of the average density of the charge.

In view of these characteristics, the Leidenfrost reactor was adopted for low-temperature polymerization of isobutylene and copolymerization of isobutylene-isoprene (butyl rubber) charges.

POLYMERS WITH SPECIAL PROPERTIES THROUGH ORDERED STRUCTURES

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The material properties of polymers depend on both the structure and morphology of the bulk polymer and on the primary structure of the macromolecules. It is a challenge to specifically control the supermolecular structure of polymeric systems by the architecture of the individual macromolecule as it is realized, for example, in biopolymers.

Macromolecules in which two different monomer units are always linked in the same way and alternate in a regular fashion along the chain are one example of polymers with tailored structures and thus materials with special properties. Access to such alternating copolymers has been considerably expanded by the concept of modifying the reactivity ratio of a comonomer pair through complexation of one of the comonomers by a third nonpolymerizable component. Aspects of polymer synthesis and tailoring of macromolecules by terpolymerization are touched on; the special properties of these ordered polymer molecules are illustrated with several examples for copolymers based on acrylics and olefins.

Segmented block copolymers with an alternating sequence of two different blocks along the chain, where either one or both blocks are characterized by distinct length, are another class of polymer materials