

Plasma-induced Polymerization

4. Low Conversion Bulk Polymerization of Styrene

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SUMMARY

Plasma-induced low conversion bulk homopolymerization of styrene was studied at room temperature. Experimental data show that a self-acceleration process, appearing due to the existence of very high molecular weight macromolecular chains, has to be considered for a kinetic approach. The presence of oxygen in the reaction milieu increases the molecular weight.

INTRODUCTION

In some previously published papers, plasma-induced copolymerizations (SIMIONESCU et al., 1980a, 1980b) and homopolymerizations (SIMIONESCU et al., 1980c) were reported. Experimental data showed that a radical mechanism of polymerization has to be considered to explain this new approach to polymer synthesis and underlined some features and advantages of plasma initiated polymerization. Thus, for example, both polymerization and copolymerization reactions led to ultrahigh molecular weight compounds. Experiments performed with styrene showed that polymers with molecular weights up to $3.87 \cdot 10^7$ were obtained.

The present paper is concerned with plasma-induced low conversion bulk homopolymerization of styrene, in an attempt to obtain more data on the mechanism of the process.

EXPERIMENTAL

Styrene was washed three times with 10% aqueous solution of NaOH to remove inhibitor, then three times with water, dried on anhydrous CaCl_2 , vacuum distilled, dried on CaH_2 , redistilled and used immediately after.

In a first experiment, the monomer was introduced in a long reaction tube, equipped with seven lateral ampoules, connected to the main tube through necks for

sealing, and with a 35 cm long and 0.8 cm interior diameter tube, connected at both extremities to the main tube and parallel to it. The monomer was frozen in liquid nitrogen, after degassing, evacuated twice to 10^{-2} Torr, and the reaction tube was sealed. An electrical discharge was then operated between two electrodes situated at 2.5 and 7.0 cm, respectively, from the sample; both were coupled to a high frequency generator (frequency - 2.5 MHz, power - 100 W). A third electrode, unconnected to the power source, was placed at 1.0 cm from the sample, in order to restrict the discharge and to impede it to touch the frozen monomer. The discharge was operated during 60 seconds. The reaction vessel was kept at room temperature. From time to time, the viscosity of the reaction system was checked by measuring the time required by a constant amount of monomer - polymer mixture to fall from an upper mark, traced on the 0.8 cm diameter tube, to a lower mark. Now and then the mixture was homogenized and part of it was introduced in one of the lateral ampoules which was detached by sealing off at the constriction with a torch, opened immediately after, and the content was diluted with benzene and precipitated in large amounts of methanol.

In a second experiment, styrene was introduced in five independent ampoules which were evacuated, but sealed before the complete evacuation of the air, in order to retain limited amounts of oxygen inside. The two electrodes were at 11.5 and 14.5 cm from the samples, respectively, and the discharge was operated during 540 seconds. The samples were kept at room temperature, opened after 170 days, diluted with benzene and precipitated in methanol.

In all cases, the obtained polymers were soluble in all solvents specific for polystyrene. The molecular weights of the samples were determined by light scattering.

RESULTS AND DISCUSSION

A large number of chemical reactions occur during the classical radical polymerization of styrene. Nevertheless, at low conversions, the kinetic scheme is simplified and the reactions of relevance are a) for initiation - initiator decomposition and initiation, b) propagation, and c) termination - by combination of the growing macroradicals (KWANT, 1979).

In the particular case of plasma-induced polymerization the initiation takes place at the very beginning of the reaction, i.e. the discharge generates the radicals which are partly consumed by reacting with monomer molecules, to produce macroradicals, and partly annihilated by mutual recombinations. A few moments after the discharge and as much as the conversion is small, the

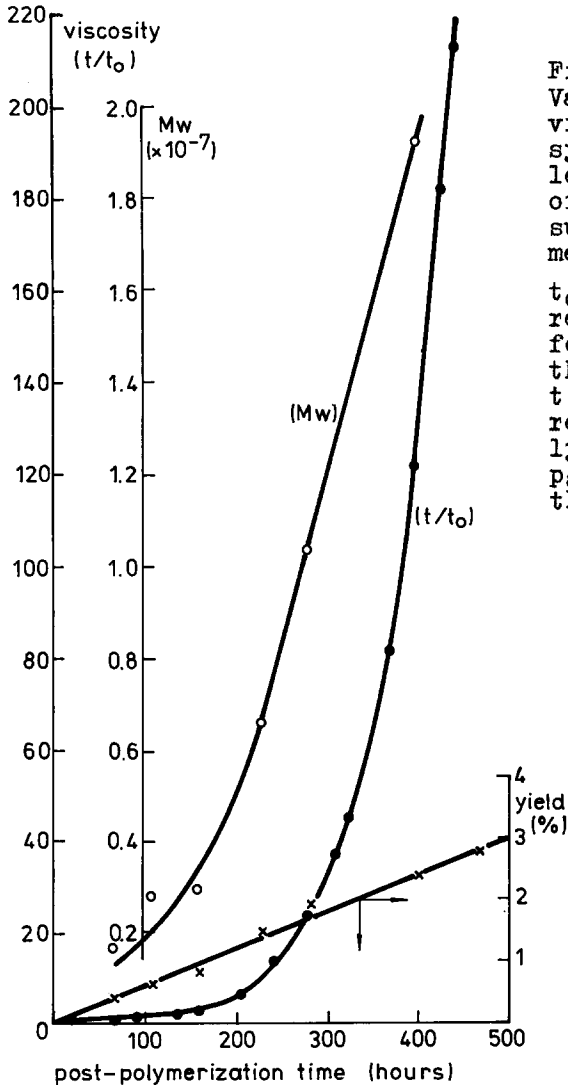


Figure 1.
Variation of the viscosity of the system, of the molecular weight and of the yield versus the post-polymerization time.

t_0 -the time required by pure monomer for passing through the two marks;
 t -the time required by monomer-polymer mixture for passing through the two marks.

only one reaction to be considered is propagation. Figure 1 presents the evolution of the viscosity of the reaction milieu, of the molecular weight and of the yield versus the post-polymerization time. One can see that both the viscosity of the system and the molecular weight of the obtained polymers strongly increase after a certain period of time. But, since the degree of polymerization is proportional to the kinetic chain length, an increased polymerization degree (or molecular weight) should also mean an increased rate of polymerization.

However, at so small conversions, the termination reactions by recombination (poly(styryl) free radicals are almost exclusively terminated by recombination) can be completely neglected, so that the rate of polymerization is, in fact, the rate of propagation. One can consider that this is a self-acceleration process, which also appears as a self-acceleration phase in bulk, solution or pearl polymerization, but at much higher conversions (Trommsdorf effect or gel effect). For instance, as concerns the bulk polymerization of styrene, this process generally occurs when the conversion has reached about 20-30%, depending on initiator concentration (ELIAS, 1977). In classical polymerizations it is an yield-depending phenomenon, appearing when the viscosity of the medium becomes very high due to conversion; as a consequence, the mobility of the macroradicals is strongly hindered and a collision between two growing chains occurs more seldom. Kinetically, the reaction rate constant of the termination decreases after the viscosity reaches a relatively high value, while the propagation rate constant increases.

In plasma-induced bulk polymerization of styrene a so important increase of the viscosity at so low conversions is necessarily due to the existence of very high molecular weight chains, and the self-acceleration process is a molecular weight-depending phenomenon. In order to demonstrate that due to the very important viscosity of the reaction system one can exclude the termination reactions, some experiments were performed with acrylic acid. This monomer was homopolymerized in bulk, by plasma-induction, and the conversion reached very quickly 100%. The macromolecular chains were proved to remain active even 60 days after the polymerization was finished: the addition of freshly distilled monomer was followed by it rapid polymerization.

The influence of oxygen traces in the polymerization medium is presented in figure 2. For all samples, the discharge time, i.e. the "initiator concentration", was the same (540 seconds), so one can consider that the same number of radicals were created in the initial phase of the polymerization process. Nevertheless the number of radicals acting as propagating species being related to oxygen (air) concentration, an increase of air (oxygen) pressure in the reaction system determines a decrease of the number of radicals (and accordingly of the number of growing chains). As a consequence, the available monomer molecules are divided between a smaller or greater number of radicals, depending on oxygen concentration, and the increase of air (oxygen) content in the milieu determines an increase of the molecular weight of the resulting polymer.

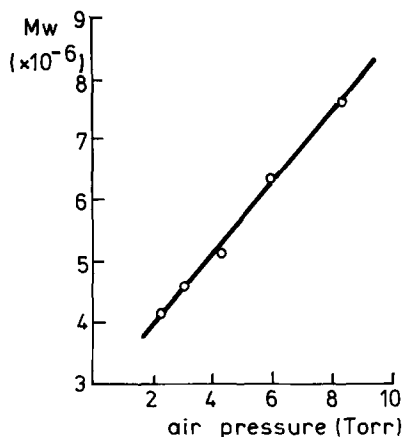


Figure 2.
Influence of air (oxy-
gen) content in the
reaction milieu on the
molecular weight of
the resulting polymer.

CONCLUSIONS

Plasma-induced low conversion bulk homopolymerization of styrene leads to very high molecular weight polymers. A self-acceleration process, appearing at very low conversions and due to the existence of ultralong chains, has to be considered on establishing the mechanism of polymerization. The presence of oxygen traces in the reaction milieu increases the molecular weight of the polymer.

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