

Use of Cyclic Di- and Triperoxides as Initiators of Styrene Polymerization at High Temperature with a View to Their Use in Industrial Applications

G. Morales¹, G. N. Eyer², J. R. Cerna¹ and A. I. Cañizo²

¹Centro de Investigación en Química Aplicada; Blvd. Enrique Reyna Herosillo 140. (25100) Saltillo, Coahuila., México

E-mail: gmorales@polimex.ciqa.mx

²Laboratorio de Química, Facultad de Ingeniería, Universidad Nacional del Centro de la Provincia de Buenos Aires, Avda del Valle 5737, (7400) Olavarría, Argentina

E-mail: neyler@fio.unice.edu.ar

Abstract: In industry, the bulk free radical polymerization of styrene takes place with the aid of peroxide initiators such as benzoyl peroxide. In this work di- and trimeric cyclic peroxides were used as initiators of the styrene polymerization in order to increase the rate of polymerization and molecular weights simultaneously.

Introduction

In the production of polystyrene (PS) various synthetic methods [1-3] such as cationic, anionic or free radical mechanisms have been applied the latter being the most important from an industrial point of view. Industrial free radical processes for the synthesis of PS generally use three reactors connected in series and the temperature is increased from 90 to 180°C reaching 60-80% of conversion. In the final step, a devolatilizer is used at temperatures of 200-220°C to recover the residual monomer. In spite of homopolymerization of styrene takes place at this temperature it is not sufficient enough to reach 100% conversion hence this step represents a problem in the economy of the process. On the other hand, the intrinsic characteristics of radical processes make it impossible to obtain high rates of polymerization and high molecular weights simultaneously.

The use of polifunctional initiators containing two or more labile groups is a way to optimize the final properties of the polymers obtained and the polymerization processes. With the aid of these type of compounds the traditional mechanism can be completely modified and high rates of polymerization can be obtained without sensibly lowering the final molecular weights of the synthesized polymers.

Experimental section

The synthesis of different polystyrenes were carried out dissolving the appropriate amount of initiator in fresh distilled styrene (0.01M). The solutions were placed into glass tubes which were evacu-

ated, sealed and kept at temperatures in the range of 90-200°C during 3 hours in order to evaluate the optimal temperature at which each of the initiators present it better performances taking into account the values of conversion and molecular weights (Mw).

The polymer samples were dissolved in THF and precipitated by adding excess methanol. This procedure was repeated several times to ensure that unreacted monomer was completely eliminated. The samples were dried in *vacuo*, and the monomer conversion was measured gravimetrically. The molecular weight and molecular weight distribution of polystyrene were determined by gel permeation chromatography using THF as a solvent. The residual monomer was analyzed by G.C injected Head Space technique. Similarly, the evolution on conversion and Mw for each of the initiators at their optimal temperature were studied at different polymerization times.

Results and Discussion

Under appropriate experimental conditions the cyclic bi- and trifunctional initiators: cyclohexanone triperoxide (CHTP), diethylketone triperoxide (DEKTP), acetone triperoxide (ATP), cyclohexanone diperoxide (CHDP) and pinacolone diperoxide (PDP) can be effectively used in styrene bulk polymerization at high temperatures to produce polymers with high molecular weights and narrow polydispersity at a high reaction rate. Varying the temperature and the initiator concentration, the free radicals concentration can be controlled throughout the sequential decomposition of the labile groups contained in the cyclic initiator molecule leading to the synthesis of polystyrene with higher molecular weights than the polystyrene produced with conventional initiators.

References and Notes

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