CHARACTERIZATION AND POLYMERIZATION OF N-ARYLMALEIMIDES

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CHARACTERIZATION AND POLYMERIZATION OF N-ARYLMALEIMIDES

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INTRODUCTION

INTRODUCTION

At the present time there is considerable interest not only in the synthesis of new types of plastic materials, but also in the modification of existing polymers in order to vary its properties to meet requirements for new applications under unusual working conditions.

Bearing these considerations in mind, it was planed to investigate the polymerization behavior and some characteristics of an interesting system having many potentialities but which did not receive enough attention in literature. This system is the N-substituted maleimides which could be polymerized either by a free radical or ionic mechanism. An obvious advantage of the poly-N-maleimides is their very stiff chain, a consequence of the 1,2 substitution. At the same time they provide an opportunity for situating bulky substituents, considerably separated from the main chain. The existence of five membered ring along the polymeric chain, with the possibility of performing hydrolysis reaction and consequently, imparting new properties to the polymer, is another advantage. Also, the 1-2-ethylenic group supplies an identical substitution for each carbon atom, and thus communicates a marked symmetry to the main chain and prevent the existence of substitutions creating weak points in the polymer backbone such as distinct bonds of the head-to-tail structure which appear in vinyl monomers. The poly N-maleimides also show a helicoidal conformation which must enhance the thermal stability (1).

A noticeable improvement of the conventional polymer could be achieved by introducing some of these remarkable N-maleimides in the polymer chain. This combination of properties could be easily achieved by the process of copolymerization of the vinyl monomer with the appropriate N-maleimide.

Therefore knowledge of the details of the process of copolymerization is of considerable interest especially it provides information on the reactivity of the different growing species towards the monomer, also it can clarify the effect of substitution on the reactivity of the monomer.

The above consideration led to the formulation of the aim of this work as follows:

Investigation of the polymerization kinetics of a selected members of N-aryl maleimides. The effect of different factors on the kinetic parameters, and on the reactivity of the monomers. In this connection the dipole moment measurement of the monomers in different solvents was chosen to throw some light on the solute solvent interaction.

The second purpose of this work was to study the different parameters affecting the copolymerization behavior and reactivity of these interesting class of monomers.

LITERATURE SURVEY

CHAPTER ONE

LITERATURE SURVEY

Since their preparation by Searle in 1948 (2) the maleimides had attracted the attention of several investigators due to the ease of preparation and the wide structural possibilities which can be achieved by varying the type of amine used with maleic anhydride.

I- Polymerization and Copolymerization of N-arylmaleimides by different mechanisms :

a) γ-rays induced polymerization

Ivanove et al (3-9) investigated, in a series of articles, the polymerization of N-arylmaleimides using γ-radiation as the free radical initiator. Polymerization was investigated under vacuum in the solid state, as well as in solution. The effect of dose rate, dose strength, temperature of irradiation, the medium and the presence of sensitizers were reported. The polymerization curves showed an autocatalytic effect, and it was found that the rate of polymerization (ν) is a function of the intensity of radiation (I), $v = KI^n$, ($n \sim 1$). The I.R. spectra of poly N-phenylmaleimide obtained by radiation were similar to those obtained by usual free radical initiator indicating the free radical nature of irradiation.

The intrinsic viscosity $[\eta]$ of the polymers increased with temperature of polymerization and decreased with radiation intensity. The curves used to determine $[\eta]$ showed anomalies characteristic of highly associated polymers. X-ray analysis of the poly-N-maleimides showed a crystalline phase for radiation initiated polymers made at low doses and that the crystallinity ratio decreased with increased dose. At high irradiation doses, the polymers obtained were amorphous and brown soluble only in DMF and swelled in CS_2. At lower doses (5 Mrad), yellow crystalline polymer soluble in DMF, and CS_2 was obtained. The authors showed, using i.r. spectroscopy, that the polymerization proceeded with opening of the c = c bond of the imide ring. The solid state radiation polymerization of the N-substituted maleimides was further investigated by a group of Japanese Scientists (10,11) in-source polymerization proceeded in a nonstationary state and the rates of polymerization were found to depend on the nature of substituents in the following order, Et > Ph = Me > Lauryl > H > p-methoxyphenyl-maleimide. The rates of post-polymerization were in the following order, Et > Me > Ph = lauryl > H > p-methoxyphenyl-maleimide. The susceptibility of N-substituted maleimides to solid state polymerization with γ-rays was different from that in the liquid state. From the x-ray diffraction studies on the polymers formed in solid state, two marked interplanar spacing were observed, the spacing of about 5 A^{o} common to all the crystalline polymers and the larger spacing which increased with the size of the substituents (11). The polymers made in the liquid state were amorphous.

A detailed characterization of poly N-phenyl-maleimide made by radiation induced solid state polymerization of the monomer was performed by Barrales-Rienda et al (12) to elucidate the influence of the radiation conditions on the conformation of the polymer. The latter authors indicated again that the I.R. spectra of polymers obtained by irradiation (^{60}Co-γ-rays) were nearly identical with those of polymers obtained by free radical polymerization in bulk or in solution. The x-ray diffractograms of all samples show two rather broad peaks indicative of noncrystalline structures. The location of the peaks do not depend upon the irradiation temperature. However, they indicated the presence of well defined short range order. It had been also suggested that, some I.R. bands in poly N-phenyl maleimide confirm the short range order proposed for packing in the solid state and were also indicative of long stereoregular chain sequences of the threo-disyndiotactic type. A similar conclusion was given before by Ivanov and his co-workers (13) who proposed a threo-diisotactic structure for poly N-p-tolyl maleimide polymerized by γ-iradiation. Barrales-Rienda et al also speculated that samples obtained at lower polymerization temperature have increased order and that this order raises the thermal stability and the average "cluster size", as a consequence of a more ordered structure of the backbone chain and hence a predominant stereoregular compound.

b) Ionic polymerization

N-phenyl maleimides and its N-4-substituted derivatives were polymerized by Na ethoxide in THF at - 78°C (14). The