

From the Mitsubishi Rayon Co. Ltd., Futatsubashi, Ushikawacho, Toyohashi, Aichiken, Japan \*), and from the Faculty of Engineering, Osaka City University, Sugimotocho, Sumiyoshi, Osaka, Japan \*\*)

## High Pressure Copolymerization of Styrene with Maleic Anhydride

By GOICHI ENOMOTO \*), YOSHIKI OGO \*\*), and TATSUYA IMOTO \*\*)

(Eingegangen am 31. März 1970)

### SUMMARY:

The radical copolymerization of styrene with maleic anhydride was investigated in an acetone solution at 40°C under high pressure up to 4000 kg/cm<sup>2</sup>. Effects of pressure on the monomer reactivity ratio considering the influence of the penultimate monomer unit were studied from kinetic data and IR spectra. It has been found that the radical copolymerization rate increases with pressure, especially concerning the reaction of maleic anhydride with a polymer chain possessing a maleic anhydride unit preceding the active styrene chain end.

### ZUSAMMENFASSUNG:

Die radikalische Copolymerisation von Styrol mit Maleinsäureanhydrid wurde in Aceton als Lösungsmittel bei 40°C unter Drücken bis zu 4000 kg/cm<sup>2</sup> untersucht. Der Effekt des Druckes auf das Reaktivitätsverhältnis der Monomeren wurde unter Berücksichtigung des Einflusses der vorletzten Monomereinheit auf Grund kinetischer Daten und der IR-Spektren untersucht. Es wurde gefunden, daß die Geschwindigkeit der radikalischen Copolymerisation mit dem Druck ansteigt, besonders bei der Reaktion zwischen Maleinsäureanhydrid mit einer Polymerkette, die vor dem aktiven Styrol-Kettenende eine Maleinsäureanhydrideinheit besitzt.

### Introduction

Radical copolymerization under high pressures has been studied by several groups of workers in recent years and the great majority of works on high pressure copolymerization have dealt with the effect of the pressure on the monomer reactivity ratio in the copolymerization system. Quantitative treatments of radical copolymerizations have generally assumed that the reactivity of a growing free radical is determined solely by its terminal monomer unit.

However it is necessary to consider that the reactivity of a growing chain in copolymerization is influenced by the nature of the penultimate monomer unit in some copolymerization systems. In an effort to determine the effect of penultimate monomer unit (penultimate effect) on copolymerization, copolymerization of styrene (S) with maleic anhydride

(M) was studied under high pressure in the present investigation since BARB<sup>1)</sup> had recognized the fact that this copolymerization system indicate the existence of penultimate effect.

### Experimental

*Styrene* was washed with 10% sodium thiosulfate solution, 10% sodium hydroxide solution and water. After drying over calcium chloride the liquid was distd. under reduced pressure (bp<sub>30</sub> 54°C).

*Maleic anhydride* was recrystallized twice from chloroform solution and dried at reduced pressure (bp 56–57°C).

*Acetone* was treated with potassium dichromate for several hrs and distd. (bp 56–57°C).

*Methanol* was distd. by the usual method.

A 54% freshly purified monomer mixture containing a given amount of acetone as solvent was filled into a glass sliding tube and then the tube was put in an autoclave at 40°C and pressurized. The pressure of the reaction system was measured by strain pressure gauge directly connected to autoclave. After appropriate time, the pressure was reduced and product removed.

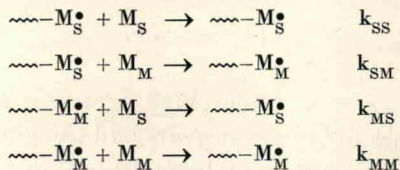
The copolymer mixture thus obtained was precipitated into a large amount of methanol as a precipitant, dried completely at room temp. and reduced pressure.

The compositions of the copolymers were calculated from the CH analysis. The IR spectra were measured at room temp. using uniform membrane of obtained copolymer.

### Results and Discussion

#### 1. Analysis of kinetic data

In the copolymerization process, there are four possible ways in which a monomer can add:



where  $\sim\sim\sim\text{-M}_S^\bullet$  and  $\sim\sim\sim\text{-M}_M^\bullet$  represents chains ending in the  $M_S$  and  $M_M$  monomer unit respectively, and where the parameters,  $r_1 = k_{SS}/k_{SM}$  and  $r_2 = k_{MM}/k_{MS}$  are defined as monomer reactivity ratios.

A copolymer composition equation which derives from the foregoing four propagating step in copolymerization cannot satisfactorily represent the experimental results in case of copolymerization with styrene and maleic anhydride system. In view of the above fact, BARB<sup>1)</sup> mentioned that a study of molecular models on copolymerization suggested the penultimate monomer unit might also be importance.