GRAFT COPOLYMERIZATION OF STYRENE-
MALEIC ANHYDRIDE AND CIS-POLYBUTADIENE

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ABSTRACT

Copolymerization of styrene-maleic anhydride in the presence of cis-
polybutadiene and toluene has been studied. The existence of various donor-
acceptor complexes in the propagation reactions has been confirmed. Attention was paid to the effect of reaction parameters (agitation speed,
polymerization temperature, initiator concentration, rubber content, MA
content) on phase inversion, and influence of addition of MA to polymeri-
ation system on structure and properties of graft copolymers.

INTRODUCTION

Rubber modified styrene-maleic anhydride copolymer, which is formed
by the dispersion of elastomer in a glassy matrix of polymer, is one class
of heterophase polymers with commercial significance after HIPS and ABS.
Rubber has the function to raise up impact strength, whereas maleic anhyd-
ride can increase the heat resistance of polymer. Since the nature of co-
polymerization of maleic anhydride and styrene tends to be alternate,
which is unacceptable for the requirements of structural materials, it is
necessary to control the sequence structure of copolymer into random form.

This paper is devoted to study such a kind of polymerization system:
during the polymerization of styrene with cis-polybutadiene dissolved in
it, a solution of maleic anhydride in toluene is dropped gradually. Poly-
merization is initiated by a free radical initiator. This is a complex
multi-component system. Attention is paid to the presence of various
donor-acceptor complexes in system, factors to affect phase inversion, and
the influence of addition of maleic anhydride to the polymerization system
on the structure and properties of graft copolymers.
**EXPERIMENTAL**

Reactor used was a 1.5 l glass reactor, with stirrer of anchor type. Rubber was dissolved in predistilled styrene under nitrogen atmosphere. After the temperature was raised to a chosen degree, initiator BPO was added. During the course of polymerization, toluene solution of MA was added through a metering pump. Before the end of reaction, a stabilizer was added. Samples were withdrawn frequently to determine the conversion degree. The product was vacuum dried at 180°C.

In the polymerization process, both quantity of toluene added and feeding rate of metering pump were maintained to be constant.

**DONOR-ACCEPTOR COMPLEXES IN STYRENE–MALEIC ANHYDRIDE–CIS–POLYBUTADIENE–TOLUENE POLYMERIZATION SYSTEM**

The mechanism of incorporation of maleic anhydride to the polymerization system of styrene has been studied extensively for many years (1). For a multi-component system comprising styrene–maleic anhydride with cis-polybutadiene and toluene, we first studied the presence of donor–acceptor complexes by the use of H' NMR.

According to the H' NMR spectra of St, MA and St+MA, when both St and MA are present in the system, the chemical shift of MA is toward high field. This verifies the formation of donor–acceptor complex of St and MA.

Similarly, we have verified that between toluene and MA, cis-polybutadiene and MA, donor–acceptor complexes are also formed.

We have used UV spectra to determine the complex equilibrium constant K of St–MA complex system. The result is 0.23 (25°C), which is in fair agreement with those from Seymour (2).

Based upon above observations, it is quite evident, St has a strong tendency to donate electron. This is why St can undertake alternate copolymerization with MA readily. However, toluene and cis-polybutadiene are also electron donors to certain extent, so they can compete with St to form complexes with MA so as to reduce the concentration of St–MA complex, and to lessen the ability of electron accepting of MA, which is favorable for the formation of random copolymer.

**COPOLYMERIZATION OF STYRENE–MALEIC ANHYDRIDE IN THE PRESENCE OF CIS–POLYBUTADIENE AND TOLUENE**