

Self-Curable Polyester by a Reaction of Glycidol with Maleic Anhydride

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ABSTRACT: The controlled reaction of equimolar quantities of maleic anhydride and glycidol in dimethoxyethane gives soluble polyesters with one hydroxyl group in each repeating unit. The reaction proceeds with stepwise ring opening of the components and gives highly viscous clear solutions in relatively short periods. In the first step, monomaleate ester formation takes place around 80 °C. The ring opening of the oxirane group is the second step, and it occurs at 120 °C. The overall reaction is the formation of soluble polyesters with moderate molecular weights (6000–18,000), without the elimination of water. The soluble polyesters can be crosslinked tightly by direct heating at 190 °C without additional vinyl monomer. © 2003 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 41: 2549–2555, 2003

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INTRODUCTION

Maleic anhydride (MA) is one of the most important compounds for the preparation of unsaturated polyesters. The presence of maleic ester segments in copolyesters provides dye reception and postcrosslinking abilities. The high electron deficiency of MA makes it capable of charge-transfer interactions. Although MA itself is a nonhomopolymerizable monomer, it forms alternating copolymers with other vinyl monomers, such as styrene¹ and vinyl acetate,² because of its charge-transfer-forming ability. Similarly, maleate ester segments in unsaturated polyesters can be copolymerized with styrene monomer to give crosslinked polymers. This reaction has a widespread application for the hardening of polyesters.^{3,4} Polyesters obtained from MA or maleic acid contain both maleate and fumarate double bonds because of the isomerization of maleic acid semiesters during polycondensation at elevated

temperatures.⁵ Because the fumarate double bond has a much greater reactivity in copolymerization with vinyl monomers, unsaturated polyesters with high fumarate contents undergo rapid crosslinking with styrene.⁶

The double bond of maleate ester, however, has a remarkable reactivity toward the nucleophilic addition of —NH, —SH, or —OH groups. The acid-catalyzed addition of hydroxyl groups to the double bonds causes the formation of branching points with ether linkages⁷ under polyesterification conditions.

The reaction of bisepoxy compounds with dicarboxylic acids to give linear polyesters has been described in the literature.⁸ This reaction has been employed for the preparation of polyesters with hydroxyl groups. This approach has also been applied to the crosslinking of hyperbranched polyacids.⁹ An interesting method related to polyester formation is the reaction of epoxy groups with cyclic anhydrides.^{10,11} The reaction proceeds without water elimination and takes place under mild conditions in the presence of tertiary amine catalysts.

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