

Kinetic and Mechanistic Studies of Homogeneous Solution Imidization

Young Jun Kim and J. E. McGrath*

Department of Textile Engineering, Sung Kyun Kwan University

* Department of Chemistry, Virginia Polytechnic Institute and State University,
Blacksburg, VA 24061

ABSTRACT

At the meeting, kinetic and mechanistic studies of the homogeneous formation of high performance polyimides will be presented. Controlled molecular weights and non-reactive phthalimide end groups were emphasized. NMR spectroscopy, non-aqueous titration and solution viscosity measurements were the principal techniques utilized. The disappearance of the amic acid groups was followed to quantitative conversion via non-aqueous titration with tetramethyl ammonium hydroxide. The homogeneous solution imidization processes were well described by auto-acid catalyzed second order kinetics. The effects of heteroatom electron donating and withdrawing bridging groups (O and SO₂) in the diamines and dianhydrides on imidization rates were investigated and a possible reaction mechanism for the solution imidization processes was proposed. Imidization of 4,4'-oxydianiline/4,4'-oxydiphthalic anhydride polyamic acid was investigated at three different temperatures (140, 150 and 180°C). Two dimensional ¹H-¹H correlation spectroscopy and intrinsic viscosity measurements provided direct evidence for partial degradation of the polyamic acid backbone structures. Complete imidization, including rehealing of the broken chains, was achieved under proper reaction conditions and the implication of these findings was considered to be very significant for the synthesis of thermally stable high performance polyimides. For polyimide systems containing benzophenone tetracarboxylic acid dianhydride (BTDA), direct evidence for network formation involving imine crosslinking, was observed by high field ¹H-NMR spectroscopy and the formation of gels was discussed as a function of reaction conditions.