다른 configuration을 가진 1,2-diaminocyclohexane이 폴리아크릴로니트릴(PAN)의 중합 거동과 입체규칙성에 미치는 영향

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Effect of the Addition of 1,2-Diaminocyclohexane with Different Configuration on the Polymerization Kinetics and Stereoregularity of Polyacrylonitrile(PAN)

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1. Introduction

The control of the stereochemistry during the radical polymerization of vinyl monomer has been a long standing concern and is still one of the most important topic in synthetic polymer chemistry.[1-5] The stereoregularity of vinyl polymers often has significant effect on the properties of polymer materials. Therefore, it is important to devise methods to control stereoregularity during the polymerization reactions. It has been reported that monomer design, reaction conditions(solvent, monomer concentration), and and additives can stereochemistry of the radical polymerization of acrylic monomers. The complex formation of monomers with Lewis acid often leads to the alteration of the polymerization reactivity and stereoregularity. In 1957, Bamford et al. first reported the increase in the polymerization rate as well as degree of polymerization of the resulting polymer during the polymerization of acrylonitrile in the presence of the lithium chloride as the Lewis acid. In this study, for the stereocontrol of polyacrylonitrile(PAN), we used 1,2-diaminocyclohexane(DACH) with different configuration, which has hydrogen-bonding interaction with nitrile group of acrylonitrile(AN).

The tacticity of PAN was characterized by NMR and FT-IR. The thermal property of PAN was characterized by DSC and TGA.

2. Experimental

2.1 Complex formation of AN/1,2-diaminocyclohexane with different configuration

AN was shaken with 10%(w/v) NaOH to extract an inhibitor, and then washed several times with distilled water and dried for 24 hr over MgSO₄. 0.1mol of AN was mixed with 0.01mol of DACH with different configuration. Interactions between AN and DACH were examined using an FT-IR.

2.2 Polymerization

Polymerization was carried out at room temperature to maintain the possibly formed complex structure between DACH and the monomer. Polymerization was carried out by photopolymerization using AIBN as an initiator.[6-8] The amine in the polymer was removed by reprecipitation and dissolution method.

3. Results and discussion

Figure 1. shows that the absorption band of nitrile groups shifts towards higher wavenumber. There coexist two peaks at 2250cm⁻¹ and 2230cm⁻¹ due to the complex formation between AN and DACH. Figure 2. shows cyclization peak of PAN polymerized in the presence of DACH with different configuration. In the presence of DACH of trans-form, cyclization peak of PAN begins from 221°C. Polymerization and characterization of the AN complexed with DACH are undergoing.

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