

## Kinetic Treatments and Thermal Properties on the Formation of Poly(ethylene 2,6-naphthalate) Polymer and its Copolyesters

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The catalyzed reaction rate and temperature dependence on the transesterification with dimethyl 2,6-naphthalate and ethylene glycol have been investigated in the presence of various metallic compounds as catalysts.

The effect of the nature and concentration for these catalysts on both reactions has been studied. The observed overall rate of the transesterification was third order; first order with respect to dimethyl 2,6-naphthalate, EG and the catalyst including initial concentration of catalyst, respectively. From the kinetic result, the decreasing order in catalytic activity on the transesterification was the order of  $\text{Pb(II)} > \text{Zn(II)} > \text{Mn(II)} > \text{Co(II)} > \text{Ti(IV)} > \text{Sn(II)} > \text{Mg(II)} > \text{Ca(II)} > \text{Na(I)} > \text{Sb(III)}$ .

The ordering of catalytic activity of metallic compound on the formation of bis(2-hydroxyethyl) naphthalate) also was found to have excellent relations to the stability constant which is indicated an index of the catalytic activity. The catalyzed polycondensation reaction of bis(2-hydroxyethyl)naphthalate were kinetically investigated in the presence of various metallic compounds as catalysts at 295°C. The effect of the type of antimony catalyst and temperature dependence on the polycondensation reaction also has been studied.

The ordering of catalytic activity on the formation of poly(ethylene 2,6-naphthalate) was found to have excellent relations to the stability constant, such as the formation of bis(2-hydroxyethyl) naphthalate). Syntheses of poly(ethylene 2,6-naphthalate) polymer also were carried out by various ligand types in antimony oxides (conc.:  $1.5 \times 10^{-6}$  mol/g BHEN) at 295°C,

and by various mole concentrations of titanium isopropoxide under the same concentration (conc.;  $1.5 \times 10^{-6}$  mol/g BIEN) of antimony catalyst. According to the results, the maximum time to reach the maximum molecular weight were largely changed. It also can be seen that the propagation and degradation rate was largely influenced by the equimolecular mixed catalyst than other mixed catalysts. The temperature dependence of BIEN with antimony triacetate as a catalyst also has been studied. From this result, it was found that the propagation rate is less influenced by a temperature change than the degradation rate.

Thermal analysis has been carried out on aromatic polyesters (i.e. poly(ethylene 2,6-naphthalate) and poly(butylene 2,6-naphthalate)) over a range of 270 to 310°C, above the melting temperature, without the addition of catalysts and stabilizers. Degradation products of polyesters were characterized by pyrolyzed gas chromatography/mass spectrometer (Py-GC/MS). It was concluded that poly(ethylene 2,6-naphthalate) decomposed by a random scission of ester links involving a six centered cyclic transition state yields vinyl naphthoate and naphthoic acid and poly(butylene 2,6-naphthalate) decomposed by two random scission of ester links gives 1-butenyl naphthoate and naphthoic acid.

Poly(ethylene 2,6-naphthalate) co-oligoesters and its copolyesters containing 1,4-butanediol (1,4-BD), 1,6-hexanediol (1,6-HD), dimethyl terephthalate (DMT), dimethylisophthalate (DMI) and dimethylphthalate (DMP) unit in polyester backbone were prepared by transesterification and melt polymerization reaction, and characterized by  $^1\text{H-NMR}$  spectroscopy. Intrinsic viscosity, glass transition temperature ( $T_g$ ), crystallization temperature ( $T_{cc}$ ), melting temperature ( $T_m$ ) and decomposition temperature ( $T_d$ ) and so on were investigated in the poly(ethylene 2,6-naphthalate) copolyesters.