

# Formation of Cyclic Oligo(ethylene Terephthalate) in Poly (ethylene Terephthalate)

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To elucidate the cyclization mechanism of poly(ethylene Terephthalate) (PET), interchange reaction rates of PET by phenethyl alcohol, benzoic acid, and benzyl benzoate were determined (Table 1). It was found that the reaction rates of phenethyl alcohol and benzoic acid were faster than that of benzyl benzoate, suggesting the occurrence of preferential cyclization at chain ends of PET. The activation energies calculated were 30.8 Kcal/mol for alcoholysis, 19.3 Kcal/mol for acidolysis, and 54.4 Kcal/mol for transesterification, respectively.

Equilibrium between PET and cyclic oligomer in benzophenone solution was found to be different from that in melt condition. Cyclic 8- or 9-mer was formed as the major component in benzophenone solution, and change of the mean square end-to-end distance of PET in the solution was suggested (Fig. 1).

Table 1. Rate constants for interchange reaction of PET

Interchange reaction	Reaction temperature ( ° C )	Rate constant ( ml /mol·min )
Alcoholysis	200	0.47
	208	0.87
	215	1.40
Acidolysis	200	1.10
	215	1.70
	230	3.32
Transesterification	210	0.10
	220	0.22
	230	1.10
	240	2.70

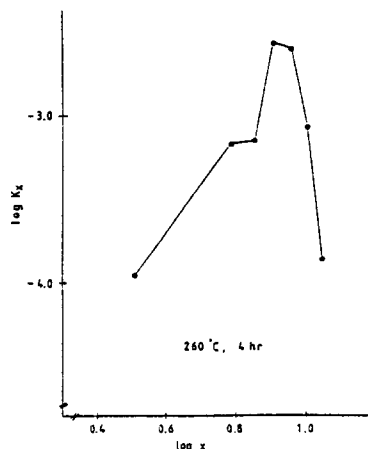


Fig. 1. Plot of molar cyclization constant,  $K_x$  against log x-mer equilibrated at 260°C in the 10% PET solution of benzophenone for 4 hr.