Control of Biodegradation of Polyesters by Molecular Design

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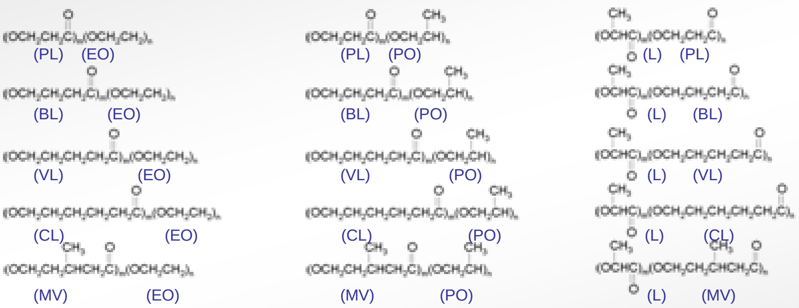
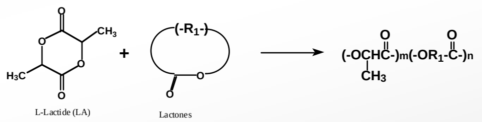
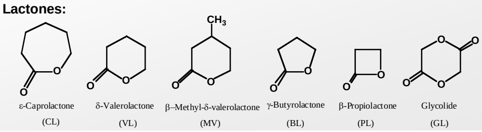
To utilize biodegradable polymers as a functional material, it is important to make the best use of their biodegradability. For improvement of reliability of biodegradation, control of biodegradation rate is indispensable, and conceivable approaches are 1) control of biodegradation by molecular design, and 2) numerical analysis of environmental parameters concerned with biodegradation. In this paper, the former study is described and the latter is explained in the other paper.

(1) Polyesters and their Derivatives

Polyesters and their derivatives were mainly synthesized by ring-opening polymerization of lactones with cyclic diesters / oxyranes / lactams. The obtained polymers were copolysters, copolyesterethers and copolyesteramides with systematic polymer composition and structural modification as follows.



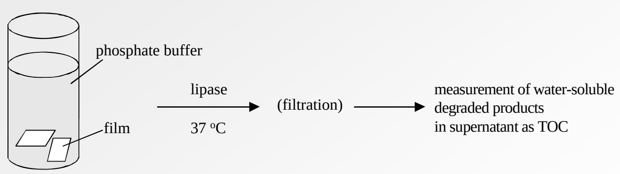




(2) Biodegradability of polyesters

Biodegradation was evaluated by enzymatic / nonenzymatic hydrolysis test, mainly. Biodegradation by an activated sludge was studied and compared with hydrolysis.

Enzymatic hydrolysis test



Effect of methyl group in ester units of copolyesterethers on enzymatic hydrolysis a)

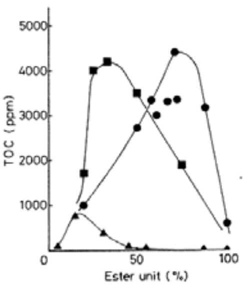
Copolymer		Tg (°C)	Tm (°C)	Δ (J / g)	TOC (ppm)	Specific TOC (TOC/α)b)
EO/G	ND	-	63	37	390	200
EO/L	18 / 82	10	59	5	40	14
EO/PL	19 / 81	-44	59	41	610	220
EO/βBL	27 / 73	-34	56	13	20	6
EO/VL	21 / 79	-	61	26	2020	460
EO/MV	13 / 87	-	-	-	20	4

a) Degradation condition: sample 25 mg, *Rhizopus arrhizus* lipase 200 unit; temp. 37 °C, time 24 hrs, phosphate buffer (pH 7.0), 2 ml.
b) α=sX/(X+Y)+tY/(X+Y), s,t: carbon numbers of oxirane and lactone units, X, Y: composition ratio of copoly(oxirane/lactone) (X/Y).

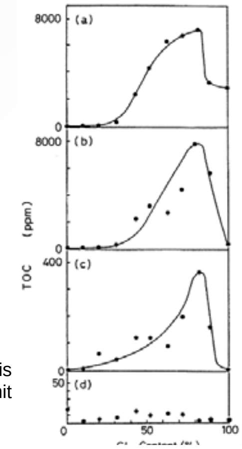
Effect of methy group in ether units of copolyesterethers on enzymatic hydrolysis a)

Copolymer		TOC(ppm)	Copolymer		TOC(ppm)
EO/βBL	50 / 50	40	PO/βBL	60 / 40	~0
	30 / 70	~0		20 / 80	~0
EO/MV	70 / 30	65	PO/MV	65 / 35	~0
	65 / 35	320		50 / 50	~0
EO/CL	50 / 50	2700	PO/CL	30 / 70	2500
	30 / 70	4400		25 / 75	2800
EO/PL	24 / 76	3000	PO/PL	23 / 77	1900

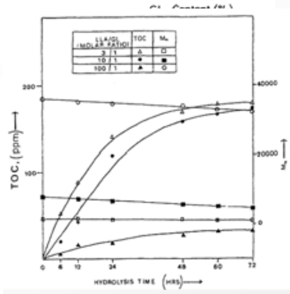
a) Degradation condition: sample 25 mg, *Rhizopus arrhizus* lipase 1250 unit; temp. 37 °C, time 48 hrs, phosphate buffer (pH 7.0), 2 ml.



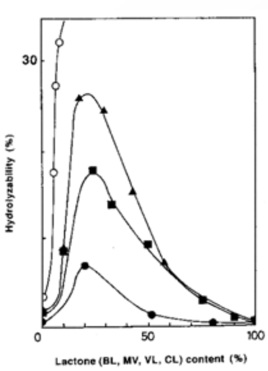
Dependence of enzymatic hydrolysis using *R. arrhizus* lipase on ester unit composition in copolyester-ethers. (●) poly(EO-*co*-CL), (▲) poly(EO-*co*-MV) , (■) poly(PO-*co*-PL) .



Enzymatic hydrolysis of poly(CL-*co*-LA)s in phosphate buffer (37℃, 24h):
a) *Rhizopus arrhizus* lipase (200U);
b)*Rhizopus delemar* lipase (200U);
c)*Candida cylindracea* lipase (200U)
(d) control.



TOC and *Mn* (GPC) values *versus* exposure time to enzymatic hydrolysis for several LA GL: glycerol.



Accelerated hydrolysis of poly(lactone-*co*-LA)s in distilled water at 70 ºC for 5 days. (●) Poly(CL-*co*-LA)s, (■) poly(VL-*co*-LA)s, (▲) poly(MV-*co*-LA)s, (○) poly(BL-*co*-LA)s.