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CATHODIC POLYMERIZATION OF VALINE N-CARBOXY ANHYDRIDES(NCA'S)

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Valine N-carboxy anhydrides(NCA's) were very smoothly polymerized with electrogenerated bases(EGB) to give the polyvalines in high yields.

Poly(amino acid)s are widely used as synthetic leathers, medicines, surface-active agents, and fibers. The most applicable synthetic method of poly(amino-acid)s is the N-carboxy anhydride(NCA) method, in which NCA's are polymerized with base catalysts.1) It is well known that the yield and quality of poly(amino acid)s are greatly affected by impurities in NCA's and kind of base catalysts used:2) since NCA's are usually prepared from amino acids and phosgene or trichloromethyl chloroformate(phosgene dimer), much efforts must be paid to remove chlorine-contaminants from the NCA's, especially in a case of amino acid such as L-valine which is polymerized with difficulty.

Recently, organic syntheses using electrogenerated bases(EGB) as reagents or catalysts have been extensively reported.3) In this communication, we wish to report that the valine NCA's could be efficiently polymerized with EGB's.

In this work, the following three methods for the polymerization of valine NCA's were comparatively examined. Method(A) was a conventional one using triethylamine(0.05 mol/mol-NCA in 60 cm^3 dry THF) as the catalyst at room temperature. In method(B), EGB's which were formed in the cathodic reduction of the NCA's themselves or supporting electrolyte(0.1 mol dm^{-3} tetrabutylammonium tetrafluoroborate in 60 cm^3 dry THF) were used as the catalyst. In method(C), α-pyrrolidone4) (0.7 mmol) as a probase was first reduced in the cathodic solution to generate an EGB and then the NCA was added to be polymerized. In methods(B) and (C) the electrolyses were carried out under galvanostatic conditions(0.08 A dm^{-2}) using a platinum cathode(12 cm^2) in a divided cell and charges required for the formation of 0.05 mol/mol-NCA EGB's were passed. The NCA's were prepared using phosgene dimer supplied from Hodogaya Chemical Co.6) and used without any special purification. As shown in Table 1, the yield of poly(L-valine) remarkably increased and the reaction time could be extremely shortened in the cathodic polymerization, particularly using the method(C). In the case of D-valine, the method(B) gave the best result, while the method(C) was found to be inferior to the other methods.

Table 1. Polymerization of Valine N-Carboxy Anhydrides(NCA) with Triethylamine and Electrogenerated Bases(EGB)

Polyvaline	Methoda)	Reaction time/h	Yield/%	$[\alpha]_D^{20}$ b) / °	Kinematic viscosityc) / 10^{-6} m^2 s^{-1}
Poly(L-valine)	A	96	17	-145	0.654d)
Poly(L-valine)	B	2	59	-120	0.670d)
Poly(L-valine)	Ce)	<0.02f)	98	-110	0.708d)
Poly(D-valine)	A	96	84	+100	0.711g)
Poly(D-valine)	B	2	93	+115	0.748g)
Poly(D-valine)	C	0.25	45	+ 94	0.699g)

a) See the text. b) Measured in trifluoroacetic acid. c) Measured at room temperature in trifluoroacetic acid (0.5 w/v%). d) Value for a standard sample(Sigma Chemical Co.) with 7200 of molecular weight, 0.616 x 10^{-6} m^2 s^{-1}. e) Charges required to generate 0.02 mol/mol-NCA EGB were passed. f) The polymerization was apparently completed in a moment when the NCA was added to the catholyte containing the EGB. g) No available standard sample.

The poly(amino acid)s thus obtained show strong absorption bands due to amino and carbonyl groups at 3290 cm^{-1} and 1640 cm^{-1}, respectively, regardless of the preparative method. This fact indicates that they have similar secondary structures.

From the above results, the cathodic methods seem to have a high potentiality in the synthesis of poly(amino acid)s. An application of this cathodic polymerization to amino acid NCA's other than valines is in progress.

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References

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4) Shono *et al*. found that the cathodic reduction of α-pyrrolidone in solutions containing quaternary ammonium salts afforded an EGB which was useful for some organic syntheses as a proton-abstracting reagent and a base catalyst.5)

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