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ENANTIOSELECTIVE PHOTOISOMERIZATION OF 1,3-BIS(9-ANTHRYL)PROPAN-1-OL IN POLY(METHYL-L-GLUTAMATE) MATRIX

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Photoisomerization(intramolecular photodimerization) of the title compound(I) proceeded enantioselectively in the matrix(II). The rate of reaction of the l-isomer is over 20% faster than that of the d-isomer. Induced circular dichroism(ICD) of I due to II matrix increased very much([θ] > 10^6) with the progress of the reaction. The origin of enantioselectivity was discussed in relation to the change in ICD.

Photochemical recognition and efficient differentiation of optically active compounds has been a dream of many researchers. If optical resolution or asymmetric synthesis is possible by simple photoirradiation without making use of expensive chiral reagents, this will benefit the understanding of asymmetric induction in prebiosynthesis as well as introduce a vast field of application. An earlier and very famous attemp was the use of circularly polarized light to introduce chirality to achiral compounds. This process called absolute asymmetric synthesis was demonstrated in the synthesis of various helicene analogues.[1] The enantiomeric excess (e.e.%) was marginal and even the highest value ever obtained was around 1%.

While there are a great number of photoreactions involving chiral compounds, reactions differentiating chirality are surprisingly scanty. Although no net chemical reactions were reported, there observed enantiomer differentiation in emission quenching processes for the combination of 1,1-binaphthyl with chiral amines[2] and tris(2,2'-bipyridine)ruthenium(II) with cobalt complexes to a modest extent.[3] Use of chiral environment has not been very successful so far. Asymmetric liquid crystals do not provide a strong driving force for enantiomer differentiation.[4]

We are now reporting the first example of efficient enantioselective photoisomerization in chiral matrix. 1,3-Bis(9-anthryl)propan-1-ol(I) known to photoisomerize in solution[5] was occuluded in a poly(methyl-L-glutamate)(II) matrix.

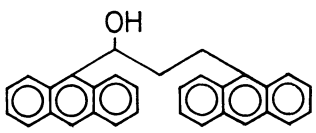

Fig. 1. Structure of 1,3-bis(9-anthryl)propan-1-ol(I).

Strong induced CD(ICD) at the ^1L_a band of I was observed. On the other hand, no such ICD was brought about in a solution containing I and II. It is therefore likely that a specific chain conformation of II around I is responsible for the ICD.

The molar ellipticity of ICD amounts to 10^5-10^6 indicating very strong coupling of the transition moment of the anthryl group with the asymmetric field of II, an auspicious sign of a favorable condition for enantioselection in a photoreaction. The anthryl groups of I underwent intramolecular photodimerization freely as shown in Fig. 2. The spectrum of anthryl groups in I is identical to that of isolated (i.e. monochromophoric) anthracene derivatives indicating the absence of preformed dimer forming site. The sandwich-like arrangement of two anthryl groups as a precursor of photodimerization is known to exhibit specific absorption different from an isolated anthryl group.[6] Consequently, the photoisomerization seems to require a certain degree of segment motion. This is supported by the fact that rigidity of the matrix examined by fluorescence depolarization of 1,6-diphenyl-1,3,5-hexatriene (degree of polarization(P) = 0.12) was found to be much less than that of poly(methyl methacrylate)(P = 0.35).

As we had hoped, enantiomer selectivity is observed when the reaction is carried out in matrix II, as shown in Fig. 2. The l-isomer is more reactive than the d-isomer by a factor of ca. 1.3, while the plots for the racemate fall in between those of the isomers. We calculated e.e.% as a function of conversion. With increasing conversion of photoisomerization, the e.e. value gradually increases as shown in Fig. 3. At a 90% conversion, the e.e. value exceeds 30%, which is extremely high for this kind of matrix-controlled reaction. Enantiomer differentiation was also confirmed by direct measurement of CD spectrum for residual I extracted with ethanol after photoirradiation.

There are several possibilities for the origin of enantioselective photoisomerization. First, there will be multiple binding sites for I in the matrix, typi-

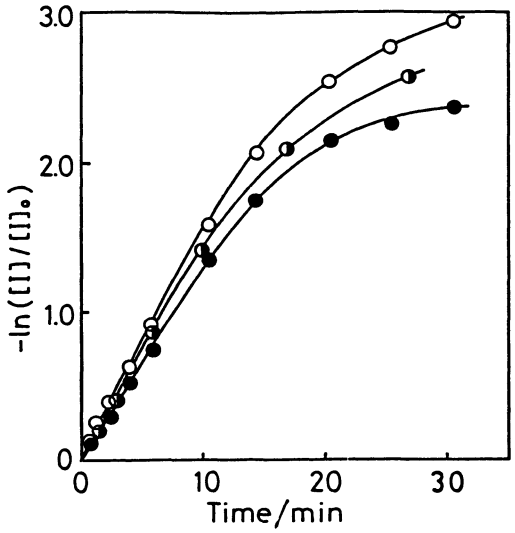

Fig. 2. First-order plots for photodimerization of I in matrix II.
●, d-isomer; ○, l-isomer; ◑, racemate.

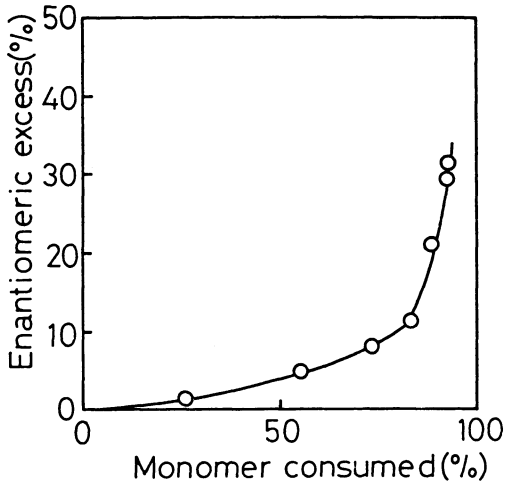

Fig. 3. Enantiomeric excess calculated from the plots of Fig. 2.

cally helix and non-helix regions. It is likely that each binding site possesses different free volume from each other, and that the rate of photoisomerization is site-dependent. As a consequence, even if the rate at a particular type of site is identical for both isomers, site-dependent photoisomerization will result in enantiomer selection. Second, provided that the matrix be uniform and homogeneous, l- and d-isomers would have different rate of photoisomerization owing to the asymmetric environment. These two possibilities may be called "static" and "dynamic" enantiomer selection, respectively. The former is based on concentration difference while the latter stems from rate difference between the isomers.

At the present stage, we cannot identify the mechanism explicitly. Nevertheless, the results of ICD change owing to photoreaction as shown in Fig. 4 support the former mechanism. The [θ] values of the isomers and racemate exceed 10^6 with progress of photoreaction. These results are explicable if we assume the presence of multiple binding sites, each providing different ICD to I. A rigid binding site would have a small free volume in which the reaction is slow whereas the ICD would be stronger. With consumption of I by photoisomerization, I becomes more and more concentrated into the rigid domain and [θ] increases. This explanation assumes that exchange of I between different kinds of sites is very slow.

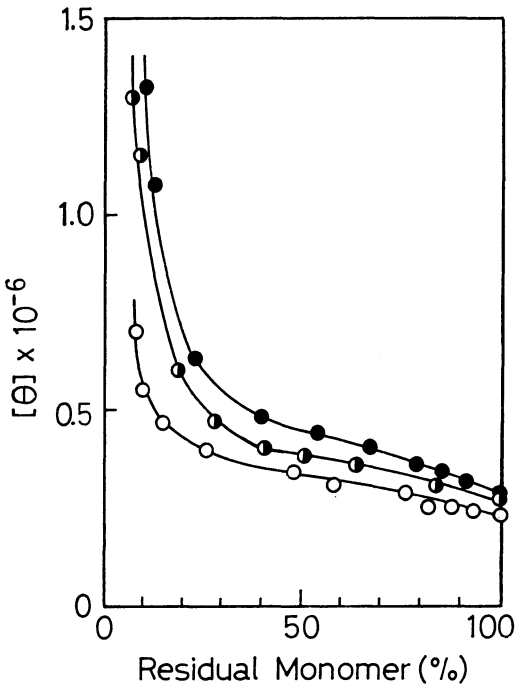

Fig. 4. Change in [θ] values during photodimerization of I.
●, d-isomer; ○, l-isomer; ◑, racemate.

We are now trying to identify the binding site which brings about strong ICD and enantiomer selection. Further details of photoisomerization, CD and ICD measurements and absolute configuration of l- and d-isomers will be published in near future.

Synthesis and optical resolution of 1,3-bis(9-anthryl)propan-1-ol(I): trans-1,3-Bis(9-anthryl)propenone prepared by coupling of 9-acetylanthracene with 9-anthraldehyde was reduced by a five times excess of $NaBH_4$ in dioxane/methanol (10/3) mixture at 75 °C for 15 min. After usual work-up, the solid product was purified by column chromatography on SiO_2(eluent: CH_2Cl_2). Recrystallization from hexane/CH_2Cl_2(1/3) gave 1,3-bis(9-anthryl)propan-1-one(5.5%) as a by-product. The mother solution was evaporated to dryness and the residue was chromatographed and recrystallized from hexane/CH_2Cl_2(2/3) to give I(79.2%). Mp 207-209 °C(lit. 207-210 °C).[7] E.A. Found: C 89.75, H 5.63%. Calcd for $C_{31}H_{24}O$: C 90.26, H 5.86%. ^{1}H-NMR: agreed.

The racemate of I was resoluted to optical isomers by preparative column

chromatography(column: CHIRALCEL ROC #2(Daicel Chem. Ind.) 2 cm x 25 cm, eluent: gradiented hexane/2-propanol(98/2→9/1), flow rate: 20 ml/min., temperature: 40 °C, monitored by UV absorption at 266 nm). The purity of d- and l-isomers was determined chromatographically as 100% and 97%, respectively. Photoreaction: Poly(methyl-L-glutamate)(II)(a gift from Ajinomoto Ltd., degree of polymerization: 1000, provided as 1,2-ethylene dichloride/perchloroethylene solution) was added with I and cast on a glass plate. The film was patched on the inside wall of a cell for spectroscopy with a minimum amount of benzene. The cell was evacuated for 12 h and sealed off. The evacuated sample was irradiated by a 300W high-pressure mercury lamp at 366 nm and the reaction was followed by UV and CD spectrometer.

Absorption, fluorescence and circular dichroism spectra were recorded on a UV-200 spectrophotometer(Shimazu), a F-4000 spectrofluorometer(Hitachi) and a J-500 circular dichrometer(JASCO).

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