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CHARGE TRANSFER COMPLEX OF POLY-γ-(β-N-CARBAZOLYLETHYL)-D-GLUTAMATE

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Two charge transfer absorption bands at 485 nm and 620 nm were observed in the system of poly-γ-(β-N-carbazolylethyl)-D-glutamate—tetranitrofluorenone dissolved in ethylene dichloride. Thermodynamic analysis and circular dichroism measurements revealed that ordering of the side chain carbazolyl chromophore occurred resulting in reordering of the α-helix main chain which had been disturbed by steric hindrance between the side chains.

We reported in the previous paper[1)] concerning charge transfer complex formation between poly-γ-(1-naphthylmethyl)-L-glutamate (PNLG) and electron acceptors. Circular dichroism (CD) observed for the charge transfer complex indicated that the α-helix content of PNLG, which is very low for non-complexed PNLG, was much enhanced by the charge transfer complexation of PNLG. It is on the other hand well-established that the bulkiness and the planarity of the carbazolyl residue attached as a substituent to the main chain of a vinyl polymer play an important role in the determination of the conformation of the polymer main chain.[2)] On the basis of the facts that the carbazolyl residue as a side chain substituent of a vinyl polymer can form a charge transfer complex and that some polymer effects were observed for the formation of the charge transfer complex of the carbazolyl residue,[3)] we set about the investigation concerning the conformation of poly-γ-(β-N-carbazolylethyl)-D-glutamate (PCDG) and its charge transfer complex with an electron acceptor.

Poly-γ-(β-N-carbazolylethyl)-D-glutamate was obtained by the ester exchange reaction between poly-γ-methyl-D-glutamate and N-β-hydroxyethylcarbazole in monochlorobenzene solution with p-toluenesulfonic acid added as a catalyst. The degree of polymerization of poly-γ-methyl-D-glutamate used was determined as 85 by viscosity measurement. Ester exchange reaction proceeded to 78.8 mole% substitution of the methyl group, and it was confirmed by viscosity measurement that no degradation of the polyglutamate main chain took place throughout the reaction.

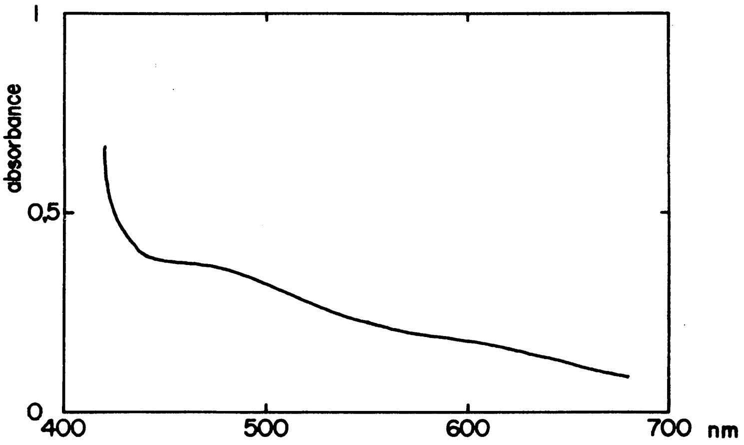

Fig. 1. Electronic spectrum of the system PCDG(4.4×10^{-4} M)–TeNF (3.8×10^{-3} M) in ethylene dichloride (optical path length: 1 cm).

The CD and the electronic spectra were taken on a JASCO J-20A spectropolarimeter and a Hitachi EPS-3T spectrophotometer. Ethylene dichloride was used after purification by fractional distillation.

Figure 1 shows the electronic spectrum of the system of PCDG and 2,4,5,7-tetranitro-9-fluorenone (TeNF). N-Ethylcarbazole is known to show two charge transfer bands with the same electron acceptor at 485 nm and at 626 nm.$^{3)}$ We can therefore assume that the bands observed for the PCDG system at 485 nm and at 620 nm are the bands due to the charge transfer transition between PCDG and the acceptor.

For the charge transfer band at 485 nm, we made a Benesi-Hildebrand plotting and obtained the equilibrium constant K. The values of entropy change, ΔS^0, and enthalpy change, ΔH^0, by the complex formation were derived from the variation of the value of K with temperature. The values obtained are listed in Table 1, along with those for the charge transfer complex of N-ethylcarbazole with TeNF. The thermodynamic values indicate that the complex formation of the carbazolyl residue is much facilitated by incorporation of the residue into the polyglutamate chain compared to that of the carbazolyl residue in the monomeric ethylcarbazole molecule. The increase in the value of $-\Delta H^0$, cancelling out the effect of the increase in the value of $-\Delta S^0$, is the cause of the enhancement of the stability of the charge transfer complex of PCDG. The entropy decrement for the PCDG complex is much enhanced from that for the N-ethylcarbazole complex. Since it was ascertained, as will be mentioned in the following, that the carbazolyl residue is restricted in its freedom in the side chain of PCDG and aligned to a considerable degree relative to the polymer main chain, this entropy decrement cannot be regarded as coming wholly from the increase in the degree of ordering of the carbazolyl residue in the side chain of the polymer, but a greater part of the decrement perhaps

Table 1. Thermodynamic parameters for charge transfer complex formation of N-ethylcarbazole (NECarb) and PCDG with TeNF

	Temp. (°C)	λ_{CT}(nm)	$\varepsilon_{\lambda CT}$	K(M^{-1})	$-\Delta H^0$(cal/mole)	$-\Delta S^0$(e.u.)
NECarb	16.1	491	2.0	7.09	3580	8.5
	22.8		2.0	5.84		
	30.1		2.0	5.32		
PCDG	19.0	485	1.1	33.9	7990	20.3
	25.0		1.1	27.3		
	31.0		1.1	19.7		

comes from the ordering of the polyglutamate main chain. Indeed, an enhancement in the helix content of the polymer by the formation of the charge transfer complex was confirmed as will be mentioned below. Perhaps, the helix conformation of the non-complexed polymer may be disturbed to a considerable extent by the introduction of the bulky carbazolyl residue into the side chain. The large decrease in enthalpy, $-\Delta H^0$, compared to that of the complex formation of N-ethylcarbazole, can also be explained by the energy gain resulting from the helix formation accompanying the complex formation.

We investigated also the circular dichroism of the charge transfer complex of the polyglutamate with TeNF. Figure 2 shows the change in the circular dichroism of the solution containing the polyglutamate and TeNF with change in the amount of the electron acceptor added to the solution. The helix content, as determined from the molar ellipticity value at 222 nm is seen to be increased by addition of and by increase in the added amount of the electron acceptor. This phenomenon on the other hand indicates that the helix structure is to some extent disturbed in the non-complexed state and that the complexation at the side chain of the polymer increases regularity of the main chain in agreement with the thermodynamic consideration of the complex formation.

As is evident from the fact that circular dichroism is observed in the visible region (Fig. 3), the charge transfer transitions are subjected to the dissymetric perturbation from the helix. This again reflects the fact that the carbazolyl chromophore in the side chain of the polyglutamate is by nature restricted in its orientation to the helix. Because of the high absorbance of the solution, we could not measure the circular dichroism for the second charge transfer band.

The carbazolyl residue in the non-complexed PCDG moleucle is demonstrated to

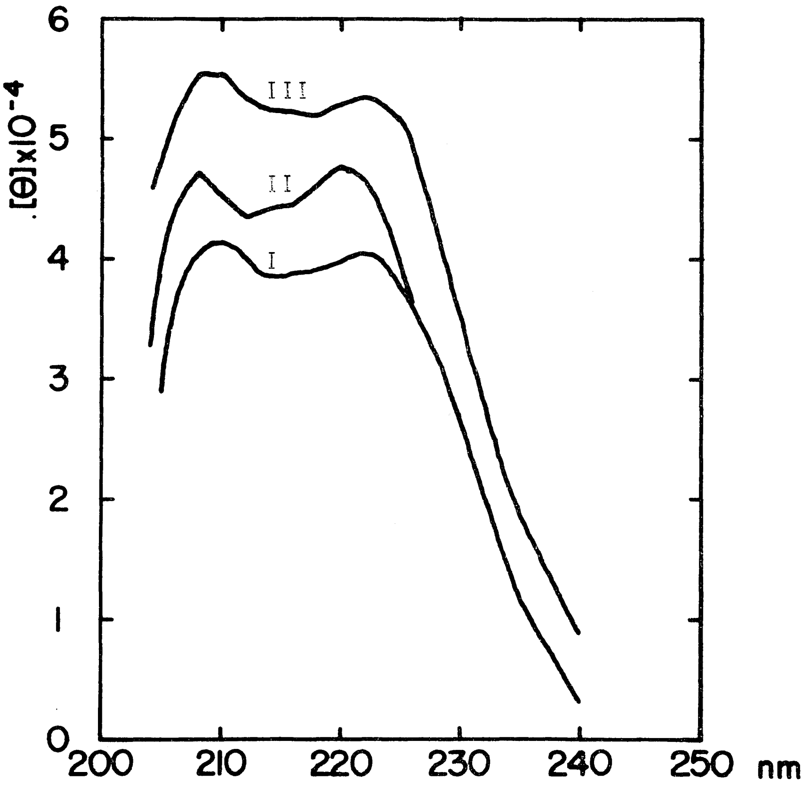

Fig. 2. CD spectra of the system PCDG(7.9×10^{-4} M)–TeNF (I, naught; II, 3.4×10^{-4} M; III, 6.7×10^{-4} M) in ethylene dichloride, [θ] calcd. on the basis of the concn. of PCDG.

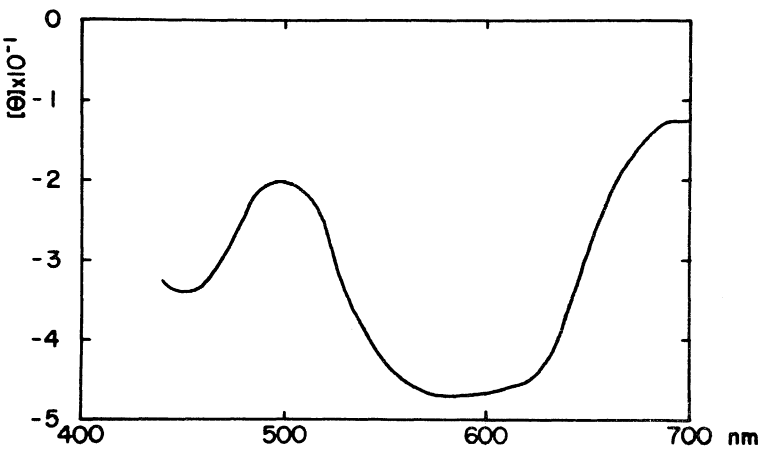

Fig. 3. CD spectrum of the system PCDG(8.7×10^{-3} M containing 6.9×10^{-3} M CDG unit)–TeNF(7.7×10^{-3} M) in ethylene dichloride, [θ] calcd. on the basis of the concn. of CDG unit.

be ordered with respect to the helix main chain by the appearance of circular dichroism for the electronic transitions of the carbazolyl chromophore. Figure 4 shows the circular dichroism spectrum in the region of the absorption of the carbazolyl chromophore for the complexed and non-complexed PCDG. The enhancement of the molar ellipticity by the complex formation is considered again as the consequence of the increase in the helix content and the enhancement of restriction of the carbazolyl chromophore by the complex formation.

The present investigation points out that PCDG molecule takes to a greater ex-

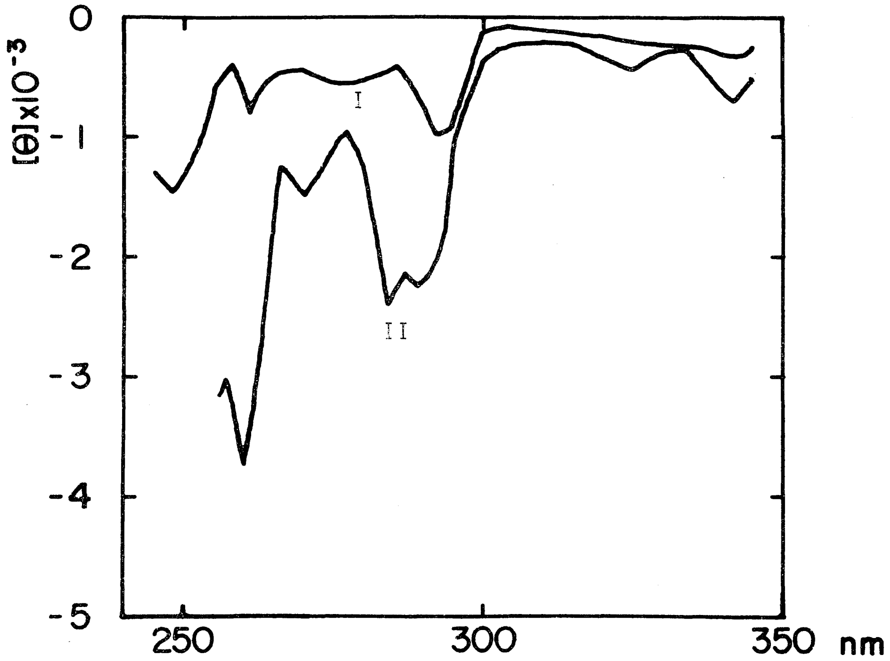

Fig. 4. CD spectra of the system PCDG(7.9×10^{-4} M containing 6.2×10^{-4} M CDG unit)–TeNF(I, naught; II, 6.7×10^{-4} M) in ethylene dichloride, [θ] calcd. on the basis of the concn. of CDG unit.

tent the α-helical conformation, and the α-helical conformation is even more enhanced by the addition of an electron acceptor molecule which can form a charge transfer complex with the carbazolyl residue in the side chain of the PCDG molecule.

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