

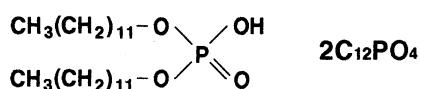
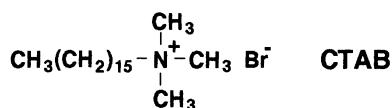
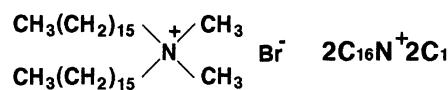
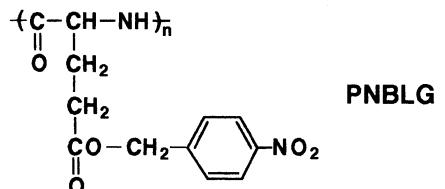
Induction of Left-Handed Helical Arrangement of 4-Nitrobenzyl Ester Residues
in Cast Film from Poly(L-Glutamate) by Using a Cationic Bilayer Forming Compound

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Poly(γ -4-nitrobenzyl L-glutamate) provided S-chirality with strong exciton coupling in cast film by using dihexadecylammonium bromide ($2C_{16}N^+2C_1$) as an additive. The X-ray and IR spectra showed that the main chain formed helices. The addition of $2C_{16}N^+2C_1$ induced a left-handed helical conformation of the main chain, along which the chromophoric residues were helically arranged.

Many poly(α -amino acid)s containing aromatic chromophores in side chains have been synthesized.¹⁻¹³ The degree of an exciton coupling in the CD around the absorption band is remarkably dependent on the flexibility of spacer chains connecting the asymmetric carbon atoms and chromophoric groups. For example, poly(L-arylalanine)s⁶⁻⁹ show much stronger exciton coupling around their 1B_b absorption bands than ester derivatives of poly(L-aspartate)^{3,10,11} and poly(L-glutamate).^{1,13} In this study, it was observed that a left-handed helix and strong exciton coupling around the 1L_a absorption band were induced in cast film from an ester derivative of poly(L-glutamate) (PNBLG) when a cationic bilayer-forming compound, $2C_{16}N^+2C_1$, was used as an additive.



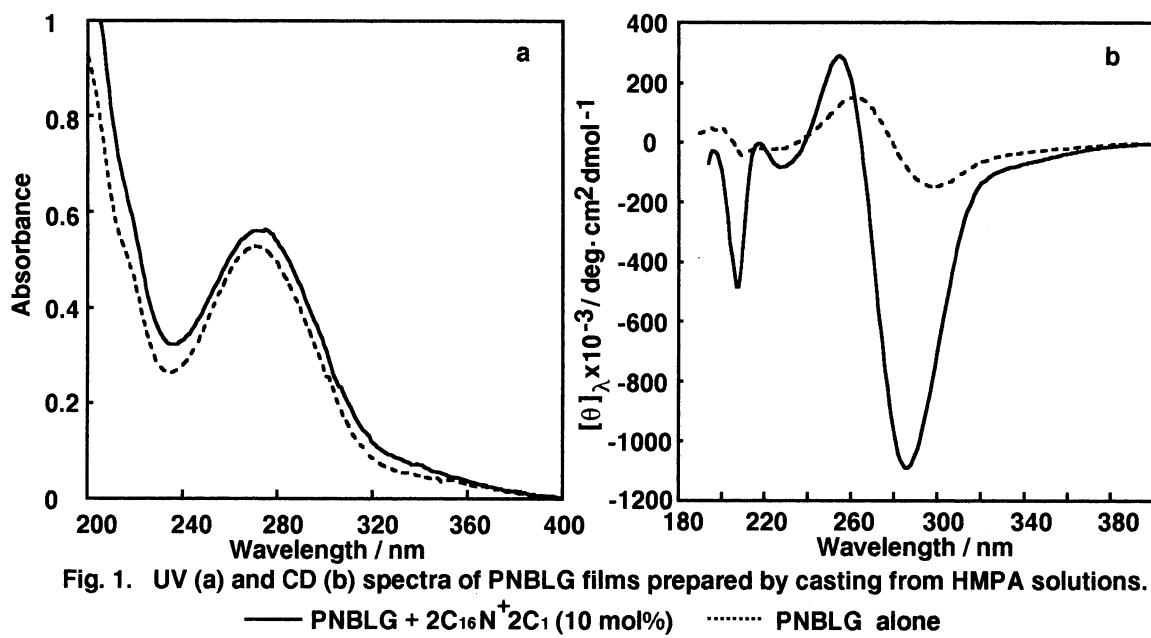


Fig. 1. UV (a) and CD (b) spectra of PNBLG films prepared by casting from HMPA solutions.

— PNBLG + 2C₁₆N⁺2C₁ (10 mol%) ······ PNBLG alone

PNBLG was obtained by transesterification with 4-nitrobenzyl alcohol in the presence of 4-toluenesulfonic acid. The chemical structure was determined by UV and NMR spectroscopy. 2C₁₆N⁺2C₁ was prepared by stepwise alkylation.¹⁴⁾ The solid film of PNBLG was prepared from PNBLG solution dissolved in hexamethylphosphoric triamide (HMPA) by casting and allowing to stand at 70 °C for 2 h.

The UV and CD spectra of the PNBLG solution were examined using pure HMPA and a tetrahydrofuran-HMPA (100 : 1) mixture as solvents. The absorption maximum is located at 270 nm in both solutions. This value corresponds to the ¹L_a absorption band of 4-nitrobenzyl alcohol (270 nm in methanol, ethanol and hexane). The CD spectra showed very little exciton coupling (about 1 × 10³ deg cm² dmol⁻¹) around the absorption band and that a right-handed helix was formed in the main chain.

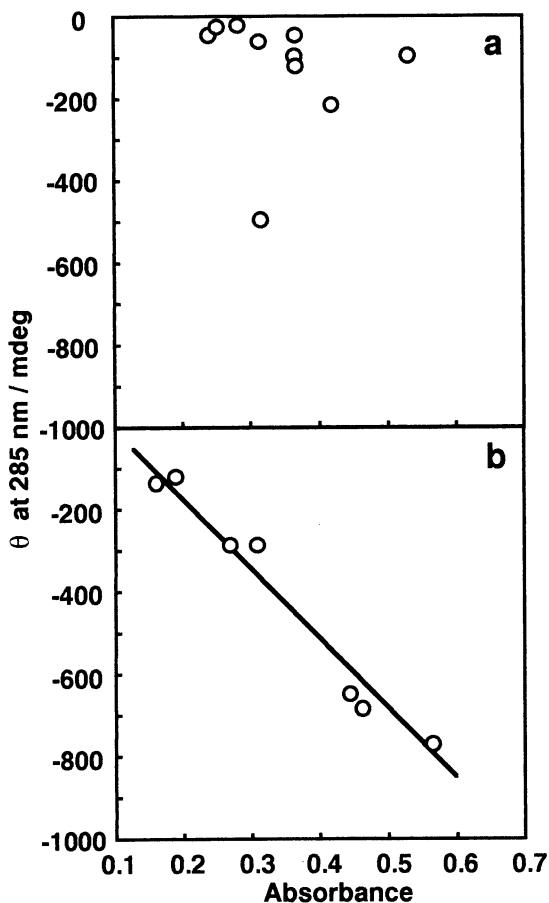


Fig. 2. Relationship between the θ value and the absorbance of PNBLG films prepared.

(a) PNBLG alone

(b) PNBLG + 2C₁₆N⁺2C₁ (10 mol%)

The UV and CD spectra in the PNBLG cast film were also examined. Fig. 1-a and 1-b show typical UV and CD spectra in the film prepared without any other additives. Stronger exciton coupling around the $^1\text{L}_\alpha$ absorption band was observed in the film than in the solution. However, the observed value of θ at 285 nm was independent of the absorption (corresponding to the thickness) of the film prepared (Fig. 2-a). This indicates that various conformations could be accidentally induced in the film. On the contrary, the cast film prepared from PNBLG containing 10 mol% of a cationic bilayer-forming compound, $2\text{C}_{16}\text{N}^+2\text{C}_1$, provided very strong exciton coupling with a good linear correlation between the values of θ and the absorption (Fig. 2-b). In addition, the value of θ at 285 nm increased to about 1000 times compared with that of the solution. The CD patterns of Fig. 1-b show S-chirality and are similar to those of poly(γ -4-nitrobenzyl D-glutamate) (PNBDG) in hexafluoro-2-propanol.²⁾ According to Konishi,²⁾ PNBDG produces left-handed helices in the solution. Similarly, Bamy et al.¹³⁾ shows that PNBLG produces right-handed helices in the solution.

X-Ray diffraction of the cast film was examined in order to determine the conformation of the PNBLG main chain. The X-ray pattern of the cast film contains sharp reflections at 13.42 (d_1), 6.66 (d_2) and 4.50 (d_3) Å. The values of d_2 and d_3 agree with those of the secondary and tertiary diffractions of d_1 . The value of d_1 is very close to the center-to-center distances (13.2 - 13.5 Å) between one of the oxygen atoms of a nitro residue and a helix from the main chain as estimated by a CPK model. Helix formation is also observed through IR spectroscopy. The IR spectra obtained using attenuated total reflection and diffuse reflection methods provide peaks in 1652 and 610 cm^{-1} in the PNBLG film, regardless of the presence or absence of $2\text{C}_{16}\text{N}^+2\text{C}_1$. The peaks are assigned to those of amide I and V lying on a helix of the main chain.

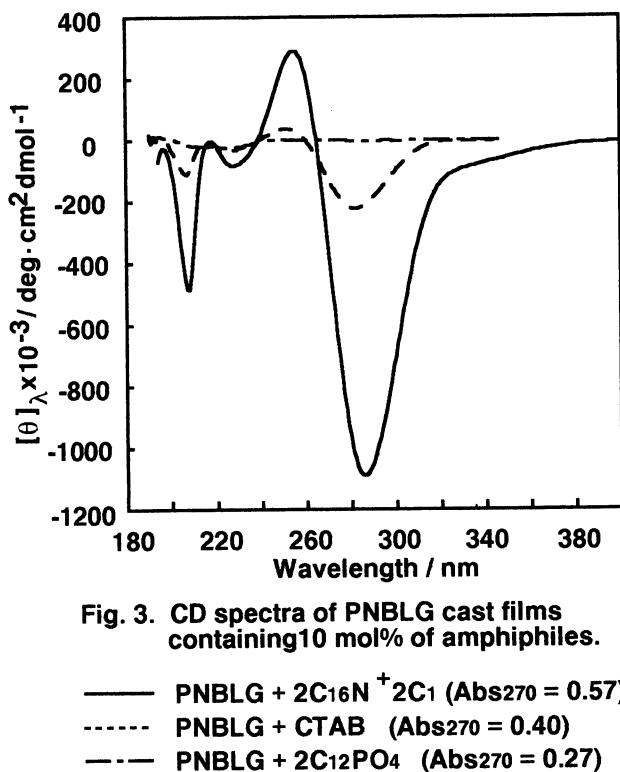


Fig. 3. CD spectra of PNBLG cast films containing 10 mol% of amphiphiles.

— PNBLG + $2\text{C}_{16}\text{N}^+2\text{C}_1$ ($\text{Abs}_{270} = 0.57$)
 - - - PNBLG + CTAB ($\text{Abs}_{270} = 0.40$)
 - - PNBLG + $2\text{C}_{12}\text{PO}_4$ ($\text{Abs}_{270} = 0.27$)

PNBLG contains a left-handed helix in the film. A strong exciton coupling around the $^1\text{L}_\text{a}$ absorption band of aromatic residues show that the chromophores are helically arranged along the main chain. Induction of a left-handed helices from ester derivatives of poly(L-glutamate) are not common. However, Sisido et al. describe the possibility of a left-handed 3_{10} -helix formation using poly(L-1-naphthylalanine)⁶⁾ and it is well-known that poly(β -benzyl L-aspartate) can form a left-handed helix in the film.¹⁵⁾ Presumably, PNBLG can form both conformations of right- and left-handed helices by evaporation of solvent from solutions, but the production ratio depends on a preparation condition. Using $2\text{C}_{16}\text{N}^+\text{2C}_1$ as an additive promotes the induction of a left-handed conformation. The cationic property and molecular orientation of $2\text{C}_{16}\text{N}^+\text{2C}_1$ were shown to be an important factor in left-handed helical arrangement of chromophoric residues, as there was almost no increase of optical activity when an anionic bilayer-forming compound, $2\text{C}_{12}\text{PO}_4$ or a micelle-forming compound, CTAB was used instead of $2\text{C}_{16}\text{N}^+\text{2C}_1$ (Fig. 3).

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