Optical Resolution of Dabsyl Amino Acids in Reversed-Phase Liquid Chromatography

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The dabsylation of amino acids has been applied to resolve their optical isomers with the use of chiral mobile phase in high performance liquid chromatography. The dabsyl amino acids were successfully separated on reversed phase column(C_{18}) by adding a chiral L-benzylproline-Cu(II) chelate to the mobile phase. The separation selectivity of the dabsyl amino acid enantiomers was not less than that of dansyl amino acids. The retention order of the dabsyl amino acid enantiomers was as those of the dansyl amino acid enantiomers except dabsyl threonine.

The optical selectivity of the dabsyl amino acids increase with pH of the mobile phase and concentration of the chelate, but slightly decreases with concentration of buffer and organic solvent composition. However serine, methionine, valine, and leucine showed a slight decrease in the optical selectivity with increase in pH. The retention times of the dabsyl amino acids decreases with increasing pH and acetonitrile concentration but increases with the concentration of the chiral chelate added. The mechanism of the optical resolution is based on a stereospecific interaction including a intramolecular hydrophobic effect and SN-2 reactivity of the ligand exchange chromatography.

It is advantageous to detect absorption at 436 nm, which is less interferent them the other detection systems. The derivatized dabsyl amino acids are stable for a month.

Introduction

Separation of optical isomers of amino acids is very important for synthesis of peptides and for the determination of the chemical structure[1]. Optical isomers of amino acids can be resolved by conversion into diastereomers. In other to carry out such a separation, an optically active agent must be present as part of either the mobile phase or stationary phase. This first attempt was carried out successfully in gas chromatography by Gil-Av and co-workers[2]. But recently, the separation of optical isomers of amino acids by using reversed phase high performance liquid chromatography has been of great interest[3-7].

There are two different methods for the optical resolution of amino acids. The one involves the use of chiral stationary phase (CSP)[8-10]. The other involves the use of chiral mobile phase additives in conjugation with achiral stationary phase[11,18]. The previous method(CSP) is particularly applicable to the separation of enantiomers when recovery of the purified isomer is desired. Davankov and his groups[9-10] used the stationary phase of L-proline attached to the resin for the separation of enantiomers of amino acids. The latter method (CMPA) has advantage capable of using less expensive conventional packings. It is easier to apply this separation system to the high performance liquid chromatography. So it has been used for the optical separation of free amino acids or amino acid derivatives[11-13]. Karger *et al.*[16,17] reported the use of L-2-alkyl-4-octyldiethylenetriamine metal complexes in aqueous mobile phases for the separation of optically active dansylated amino acids(DNS-AA). Hara and Gil-Av(24) successfully separated free amino acids by use of a proline-Cu(II) eluent on an ion exchange column.

In this paper, we tried the optical resolution of dabsyl amino acid (DABS-AA) on a C_{18} column by adding the chiral chelate of Cu(II)-N-benzyl-L-proline to the mobile phase. The resolution of optical isomers of dabsyl amino acids is compared with that of dansylated amino acids. The different elution behaviors between DNS-AA and DABS-AA are illustrated based on the ligand exchange reaction and hydrophobic interaction which show the stereoselectivity during the chromatographic elution.

Experiments

Instrument. The liquid chromatograph from Waters Associates consisting of Series 440 absorbance detector, Model 6000 A solvent delivery system, Model U6K LC injector and Model 730 Data Module was used for this work. The UV detector was set at 436 nm. The mobile phase flow rate was 1.0 m*l*/min at a pressure of about 1500 psi. The column was μ-Versapack C_{18}(30 cm × 4.1 mm i.d.). The pH of the mobile phase was adjusted by a pH meter(Model 292) of the Fisher Scientific Company.

Reagents. Dabsylation was done through the precolumn derivatization of free amino acids to enhance the detectability and to see the optical separation. Free amino acids such as D, L-valine(Val), D,L-asparagine(Asn), and D,L-tyrosine (Tyr) were obtained from Sigma Chemical Co., (St. Louis, Mo, U.S.A.). D, L-leucine(Leu), D,L-phenylalanine(Phe), D,L-threonine(Thr), and D,L-methionine(Met) was obtained from Yoneyama(Osaka, Japan). Dabsyl chrolide(DEBS-Cl) was obtained from Dojido Laboratories (Kumamoto, Japan). The dry amino acids were dabsylated according to the precedure described below[25,26]. A 1 m*l* dabsyl chloride solution (0.65 mg/m*l* in acetonitrile) was mixed with 1 m*l* of 0.1 M sodium bicarbonate solution containing free amino acids. The reaction mixture was shaken in water bath at 70 °C for 30 minutes when the red color of DABS-Cl was changed to orange color. The resulting solutions were directly introduced to the injector of the liquid chromatograph for the separation.

The ligand, N-benzyl-L-proline(BzPro), was synthesized by treating L-proline with benzyl chloride under a basic condition[27-29]. The product was identified by UV, IR, ^{1}H and ^{13}C NMR spectra. The yield was 58%, N-benzyl-L-proline was used as the ligand for the copper(II) chelate. The mobile

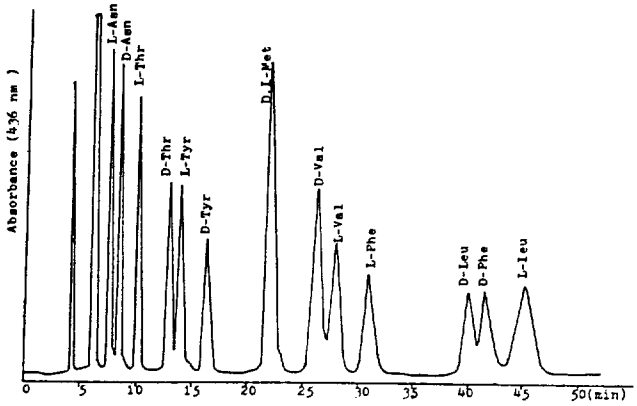

Figure 1. Typical chromatogram of DABS-amino acids with chiral mobile phase addition method. The mobile phase containing 35% acetonitrile and 65% 5×10^{-3} M chelate solution containing 2×10^{-2} M NH_4Ac buffer at pH 6.5. The chelate is Cu(II)-$(BzPro)_2$.

phase containing N-benzyl-L-proline and Cu(II) with 2:1 molar ratio was used for the resolutions of optical isomers of DABS-amino acids, and adjusting the pH to the desired value with acetic acid or sodium hydroxide solution. Mobile phase were degassed and purified by a solvent clarification kit just before use.

Results and Discussion

The separation of the optical isomers of derivatized amino acids for all these compounds is of interest because the elution orders between D and L derivatized amino acids are different from those obtained in the use of different ligands such as L-proline, L-hydroxyproline, N-benzyl-L-proline, N-benzyl-L-hydroxyproline, and N-xylenylproline[20,21,29-31]. However, the elution orders of the dabsylated amino acids were the same as three of the dansylated amino acids except DABS-threonine as shown in Figure 1. On the other hand, the elution order for DABS-threonine enantiomers were reversed compared with DNS-threonine. This behavior indicates that the relatively long chain of dabsyl group affects differently for the resolution of DABS-amino acids relative to the short chain of naphthyl group in DNS-amino acids. The retention behaviors for separation of the DABS-amino acids can be illustrated on the stereospecific interaction of the ligand exchange reactions. The capacity factors of DABS-amino acids and the separation selectivity of their enantiomers varied with the pH of the mobile phase as shwon in Table 1. The capacity factors of DABS-amino acid enantiomers decreased with pH of the mobile phase. This behavior was the same as that of DNS-amino acids. The decrease of the capacity factor on pH indicates that the binary complexes are more stable than the ternary with increase in pH due to the greater deprotonation of the ligand and thus the ligand exchange reaction with DABS-amino acids under these conditions seems much more difficult. We believe that the optical selectivity increases with increasing pH because of difference in stereospecificity coming from the ligand exchange reaction. The optical resolution of the DABS-amino acids is also dependent on the concentration of the copper(II)-N-benzyl-L-proline chelate added as shown in Table 2. The capacity factor and selectivity of the optical isomers of DABS-amino acids increased as the concentration of the chrial chelate additive increased. The increase of capacity factors with increasing the chelate concentraiton indicates that the ternary complexes retain longer than the corresponding binary complex. The increase of the optical selectivity with increase in the concentration of the ternary chelate indicates that the hydrophobic interaction of the ternary complexes with the stationary phase shows enantioselectivity.

The effect of concentration of acetonitrile on the retention behaviors is shown in Table 3. It show that the lower the concentration of acetonitrile, the greater is the retention of the isomers as expected in reversed phase high performance liquid chromatography. The selectivity between the dabsyl enantiomers with increasing acetonitrile concentration was little affected unlike the dansyl amino acids[29]. Therefore, it seems that there are some difference in the conformation of

Table 1. Capacity Ratio(k') and Selectivity(α) as a Function of pH

DABS-AA		pH 6.0 k'	pH 6.0 α	pH 6.5 k'	pH 6.5 α	pH 7.0 k'	pH 7.0 α	pH 7.5 k'	pH 7.5 α
Ser	D	1.03	1.08	0.89	1.06	0.96	1.05	1.10	1.04
	L	1.11		0.94		1.01		1.14	
Asn	D	1.00	0.98	0.92	0.93	1.03	0.89	1.29	0.84
	L	0.98		0.86		0.92		1.09	
Thr	D	1.58	0.92	1.31	0.85	1.30	0.85	1.50	0.77
	L	1.45		1.11		1.10		1.15	
Tyr	D	2.30	0.83	1.77	0.80	1.68	0.77	1.78	0.71
	L	1.90		1.42		1.29		1.26	
Met	D	3.38	1.07	2.61	1.04	2.53	1.06	2.77	1.00
	L	3.63		2.72		2.67		2.78	
Val	D	4.38	1.14	3.06	1.11	2.83	1.11	2.77	1.07
	L	5.01		3.39		3.15		2.96	
Phe	D	6.52	0.82	4.78	0.78	4.54	0.74	4.77	0.69
	L	5.33		3.71		3.36		3.31	
Leu	D	6.87	1.17	4.74	1.15	4.37	1.18	4.31	1.14
	L	8.06		5.44		5.15		4.92	

35% Acetonitrile and 65% Cu(II) chelate solution containing 5×10^{-3} M Cu(II)-$(BzPro)_2$ is mobile phase. The ammonium acetate buffer concentration was 2.5×10^{-2} M. The flow rate is 1.0 ml/min.

Table 2. Capacity Ratio(k') and Selectivity(α) as a Function of Complex Concentration

DABS-AA		1.0×10^{-3} M k'	α	5.0×10^{-3} M k'	α	10×10^{-3} M k'	α
Ser	D	0.95	1.02	0.88	1.07	0.14	1.25
	L	0.97		0.94		1.43	
Asn	D	1.00	0.94	0.90	0.94	1.12	0.94
	L	0.94		0.85		1.05	
Thr	D	1.13	0.89	1.32	0.84	1.76	0.86
	L	1.01		1.11		1.52	
Tyr	D	1.65	0.81	1.80	0.81	2.62	0.76
	L	1.34		1.45		2.00	
Met	D	2.41	1.03	2.66	1.04	3.80	1.07
	L	2.49		2.76		4.05	
Val	D	2.19	1.02	3.12	1.10	5.29	1.25
	L	2.24		3.43		6.61	
Phe	D	4.12	0.81	4.94	0.78	7.77	0.74
	L	3.34		3.84		5.72	
Leu	D	3.54	1.04	4.91	1.14	8.26	1.29
	L	3.71		5.59		10.65	

35% Acetonitrille and 65% Cu(II) chelate solution containing 5×10^{-3} M Cu(II)-$(BzPro)_2$ is the mobile phase. The ammonium acetate buffer concentration was 2.5×10^{-2} M at pH 6.5. The flow rate is 1.0 m*l*/min.

Table 4. Capacity Ratio(k') and Selectivity(α) as a Function of Buffer Concentration.

DABS-AA		1.0×10^{-2} M k'	α	2.0×10^{-2} M k'	α	3.0×10^{-2} M k'	α
Ser	D	1.00	1.05	0.98	1.08	0.97	1.09
	L	1.05		1.06		1.06	
Asn	D	1.02	0.93	1.02	0.92	1.04	0.90
	L	0.95		0.94		0.94	
Thr	D	1.58	0.84	1.51	0.88	1.45	0.83
	L	1.33		1.33		1.20	
Tyr	D	2.23	0.68	2.21	0.76	2.00	0.78
	L	1.52		1.67		1.56	
Met	D	2.48	1.41	3.18	1.08	2.93	1.05
	L	3.50		3.43		3.07	
Val	D	4.10	1.16	3.99	1.15	3.39	1.09
	L	4.77		4.58		3.69	
Phe	D	6.08	0.72	6.23	0.75	5.59	0.75
	L	4.38		4.67		4.18	
Leu	D	6.32	1.25	6.27	1.20	4.99	1.22
	L	7.87		7.51		6.08	

35% Acetonitrile and 65% Cu(II) chelate solution containing Cu(II)-$(BzPro)_2$ at pH 6.5 is the mobile phase. The flow rate is 1.0 m*l*/min.

the DABS-amino acids compared with those of DNS-amino acids due to the long dabsyl group.

Separation of the optical isomers of DABS-amino acids is also slightly dependent on the concentration of buffer in the mobile phase as shown in Table 4. The capacity factors of DABS-amino acids and their optical selectivity slightly decreased as the concentration of ammonium acetate in the mobile phase increased. This behavior can be explained that acetate ion as well as benzyl proline as a ligand is competitive to the binary chelate. So the decrease in the concentration of the ternary complexes resulting from increase in acetate ion decreases the retention and the optical selectivity as sell.

Several models[24,30-36] which illustrate the separation mechansm of the optical isomers have been suggested. The separation of the optical isomers of the DABS-amino acids can be explained with a *cis-trans* reaction mechanism for the optical separation of DABS-amino acids. It can be suggested that two molecules of N-benzyl-L-proline be bounded to Cu(II) to form five membered ring[32] and the copper chelates resulted are well known as square planar[37] to have a *trans* or *cis* configuration. The *trans* configuration of

Table 3. Capacity Ratio(k') and Selectivity(α) an a Function of Acetonitrile Concentration

DABS-AA		32.5% k	α	35.5% k'	α	37.5% k'	α	40.0% k'	α
Ser	D	1.02	1.03	0.91	1.14	0.67	1.07	0.53	1.08
	L	1.05		1.04		0.72		0.57	
Asn	D	1.08	0.90	0.95	0.94	0.72	0.92	0.56	0.96
	L	0.97		0.89		0.66		0.54	
Thr	D	1.56	0.83	1.26	0.87	0.95	0.89	0.73	0.89
	L	1.29		1.09		0.85		0.65	
Tyr	D	2.13	0.82	1.52	0.99	1.22	0.82	0.97	0.76
	L	1.73		1.51		1.00		0.74	
Met	D	3.22	1.02	2.80	1.18	1.98	1.06	1.46	1.07
	L	3.29		3.31		2.09		1.56	
Val	D	3.67	1.10	3.14	1.23	2.32	1.13	1.71	1.13
	L	5.98		5.35		3.58		2.54	
Phe	D	5.98	0.77	5.35	0.80	3.58	0.77	2.54	0.78
	L	4.59		4.26		2.74		1.98	
Leu	D	5.84	1.12	4.22	1.44	3.55	1.16	2.56	1.18
	L	6.56		6.09		4.13		3.03	

The added chelate solution is 5×10^{-3} M Cu(II)-$(BzPro)_2$. The ammonium acetate buffer concentration was 2.5×10^{-2} M at pH 7.0. The flow rate is 1.0 m*l*/min.

DABS-amino acids and copper binary complexes is believed to have higher enantioselectivity than the *cis* form due to the symmetric configuration. So it can be assumed that the *trans* forms of the binary complexes are prevalent in the mobile phase.

The side chains in the dabsyl amino acids seem to have an intramolecular hydrophobicor hydrophillic interactions with the dabsyl group to form a dominant conformation[29-31]. The intramolecular interactions of the dabsyl amino acids seem to be more feasible than those of the dansyl amino acids due to the relatively long dabsyl group.

It has been believed that the ligand exchange reaction occurs as follows.

$$(BzPro)-Cu(II)-(BzPro)+DABS-AA \overset{k}{\rightleftharpoons}$$

$$(BzPro)-Cu(II)-(DABS-AA)+BzPro$$

The equilibrium constants of D-isomers are not identical with those of L-isomers because of the difference in enantioselectivity for the ligand exchange reactions in the mobile phase. The retention behaviors of the DABS-amino acids can be expalined by the proposed mechanism reported from the previous results[21,29].

It can be suggested that the optical isomers of DABS-amino acids have an exchange reaction with the copper(II)-$(BzPro)_2$ chelate by a SN-2 reaction. The ligand exchange of the binary complexes (Cu(II)-$(BzPro)_2$) with D- or L-DABS amino acids have a enantioselectivity to exhibit the separation of the enantiomers. L-DABS-amino acids are able to attack the Cu(II)-$(BzPro)_2$ chelate to produce the ternary complexes consisting of both *cis* and *trans* configurations without the steric hindrance, while D-DABS-amino acids are able to attack the Cu(II)-$(BzPro)_2$ chelate to form the ternary complexes of *cis* configuration but hardly to form those of *trans* configuration due to the steric hindrance of the five membered ring of L-benzyl proline with the dabsyl group of the DABS-amino acids. Therefore, the L-DABS amino acids are more retained than D-DABS amino acids because the ternary complexes of L-DABS amino acids retain much more than those of D-DABS amino acids.

However, the elution orders between D- and L-DABS-amino acids in case of DABS-Asn, DABS-Tyr, an DABS-Phe were reversed as known from the results of the dansyl amino acids[29-31]. It seems to have a greater hydrophobic interaction of the *cis* products resulted from L-forms because the prolyl group of the chelate has a same plane with the dabsyl group and side chain of the DABS-amino acids. It can be speculated that the bulky groups of the three rings on the same plane have a strong hydrophobic interaction with the reversed stationary phase.

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Synthesis and Electrical Conductivities of Poly(1,4-phenylenevinylene-co-2,3,5,6-tetramethyl-1,4-phenylenevinylene)s

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A series of copolymers of poly(1,4-phenylenevinylene-co-2,3,5,6-tetramethyl-1,4-phenylenevinylene), poly(PV-co-TMPV), were prepared in film forms from the precursor polymer films. The sulfonium salt precursor polymers were synthesized by copolymerization of the mixtures of the respective bis(sulfonium salt) monomers. All of the copolymer films could be doped with $FeCl_3$ to have high electrical conductivities and they showed good air stability. The maximum conductivity of the $FeCl_3$-doped films ranged 10^{-3} to $10^2 Scm^{-1}$ depending on the composition of the copolymer films. However, these copolymer films could not be doped with iodine. The coplanarity of PV and TMPV units in the main chain appears to be affected by steric effect of the methyl groups in the TMPV units.

Introduction

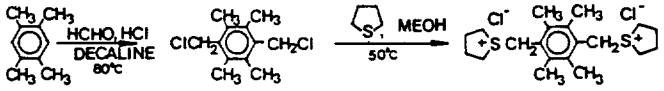
The synthesis of poly(1,4-phenylenevinylene), PPV, and its derivatives and copolymers through the water-soluble precursor route[1-7] is one of the most promising methods to obtain the polymers with extended π-conjugated structures. The PPV derivatives are attracting much interest as new conductive materials and materials for non-linear optics[8-11] because they can be obtained as dense, tough and flexible films and show superior chemical stability. The precursor route has been applied to the preparations of poly(2,5-dimethoxy-1,4-phenylenevinylene)(PDMPV)[4], poly(2,5-thienylenevinylene)(RTV)[5] and their copolymers.[6]

The PPV films obtained in this manner can be easily doped with strong oxidizing agents such as AsF_5 to produce highly conducting materials, but they can not be effectively doped with I_2.[2] Doping PPV films with AsF_5 results in conductivities of 10-40 Scm^{-1} for unstretched samples and 500-3000 Scm^{-1} for uniaxially stretched ones.[2,3,12] In contrast, the PPV derivatives such as PDMPV and its copolymers show easy dopability to I_2 leading to high conductivities. For example, the I_2-doped PDMPV exhibits an electrical conductivity in the order of 10^2 Scm^{-1} at room temperature. The high conductivities observed for doped PDMPV can be attributed to the electron-donating capacity of the methoxy groups on the phenylene group. They lower the oxidation potential of the conjugated polymers.[13]

In the preparation of these polymer films, water-soluble sulfonium salt precursor polymers of high molecular weight are first prepared and cast into films. They are then subjected to thermal elimination to the final polyconjugated polymers. If desired, the precursor films can be uniaxially drawn before or during the thermal elimination reaction. Oriented films show a significantly enhanced conductivity on doping along stretched direction.[14,15,20]

Recently, we prepared poly(2-methoxy-5-methythio-1,4-phenylenevinylene)(PMMPV) and its copolymers,[14] and poly(2-*n*-butoxy-5-methoxy-1,4-phenylenevinylene)(PBMPV)[15] via the corresponding water-soluble precursor polymers. These polyconjugated polymers could be readily doped with oxidizing dopants such as I_2, $FeCl_3$ and $Fe(ClO_4)_3$ to produce materials having a wide range of conductivities depending on the nature of substituents and dopants. In the case of PBMPV, I_2-doped films exhibited conductivities as high as 590 Scm^{-1} and $FeCl_3$-doped ones as high as 2160 Scm^{-1}. The films could be stretched up to a draw ratio of 4-8 before the final elimination.

In this paper, we describe the synthesis of a series of poly(1,4-phenylenevinylene-co-2,3,5,6-tetramethyl-1,4-phenylenevinylene)s, poly(PV-co-TMPV), using different mole ratios of the two respective sulfonium salt monomers in polymerization. The copolymers in film forms were doped with $FeCl_3$ and their electrical conductivities were measured. It was our purpose to learn more about the substituent effect on the electrical properties of PPV derivatives. The synthetic route and the structure of poly(PV-co-TMPV)s prepared and characterized in this investigation are shown below;



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