Redox-active polymers: synthesis and exchange reaction of amino compounds containing a cyclic disulfide

Mario Casolaro* and Elena Busi
Dipartimento di Chimica, Università di Siena, Piano dei Mantellini 44, 53100 Siena, Italy
(Received 29 March 1993)

Two monoamidated amino compounds, bearing the cyclic disulfide moiety of lipoic acid, were prepared by imidazole group transfer with aliphatic diamines (1,3-diaminopropane and piperazine). The products, characterized by spectroscopic methods (^{1}H nuclear magnetic resonance and Fourier-transform infra-red), were studied in solution. Basicity constants for the protonation of the basic nitrogens were evaluated in aqueous media, and redox properties in dimethylsulfoxide, by cyclic voltammetry. Insoluble polymers were obtained by polymer-analogue exchange reaction of the monoamidated compound with a benzotriazole residue present in preformed poly(*N*-acryloylbenzotriazole). A copolymer of the same monomer with *N*-vinylpyrrolidinone was soluble in solvents, giving a response in cyclic voltammetry. Its positive anode peak was slightly higher than that of the simple monoamidated compounds.

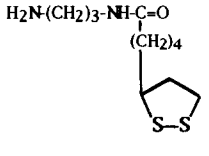
(Keywords: redox polymer; lipoamide–amine; exchange reaction)

INTRODUCTION

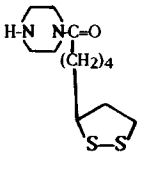
A class of reagents containing redox-active moieties is based on compounds that have the five-membered disulfide ring of lipoic acid and its derivatives[1–3]. These compounds, with an –S–S– bond, are used as precursors to introduce –SH groups into polymers, improving the powerful reducing character for disulfide bridges in proteins[4]. Moreover, selective reduction of organic molecules can be obtained by polymer-supported catalysts based on dithiol-iron(II) complexes[5].

The synthesis of reactive polymers by polymerization of the corresponding vinyl monomers carrying functional groups may be difficult or even impossible, especially if the desired function retards or interferes with the radical polymerization process[6]. A way to obtain polymers with specialized functions was reported by Ferruti *et al.*[7–9]. It is an indirect route based on the exchange of amines, bearing the desired groups as substituents, with the benzotriazole residue on preformed poly(1-acryloylbenzotriazole)[7,10].

The aim of this paper was to prepare two new amino compounds bearing the cyclic disulfide:



1



2

obtained by monoamidation of lipoic acid with bis-primary (1,3-diaminopropane) and bis-secondary (piperazine) amines. The aminolipoyl derivative was inserted in a polymer matrix by exchange reaction with the benzotriazole residue. The redox properties of a soluble copolymer (*N*-vinylpyrrolidinone-*co*-1-acryloylbenzotriazole) incorporating **1**, evaluated by cyclic voltammetry, were compared with those of the corresponding low-molecular-weight analogues.

EXPERIMENTAL SECTION

Materials

α-Lipoic acid and 1,1′-carbonyldiimidazole were purchased from Fluka and used without further purification. *N*-Vinylpyrrolidinone (from Fluka) and acryloyl chloride (from Aldrich) were distilled under reduced pressure before use. Chloroform (from Baker) was repeatedly washed with double-distilled water and dried over CaF_2. Anhydrous piperazine (from Ega-Chemie), 1,3-diaminopropane (from Aldrich) and triethylamine (from C. Erba) were used as received.

Spectroscopic measurements

^{1}H n.m.r. was performed at 200 MHz on a Bruker AC 200 spectrometer in deuterated dimethylsulfoxide (DMSO-d_6) using tetramethylsilane (TMS) as internal reference. *FT*i.r. spectra were run on a Perkin–Elmer M1800 spectrophotometer from KBr pellets (powdery compounds) and a.t.r./*FT*i.r. spectra from films (rubbery compounds).

Potentiometric and viscometric measurements

Potentiometric titrations were carried out at 25°C in 0.1 M NaCl by a previously described procedure[11] using computerized analytical devices (Radiometer PHM-84 and Multidosimat piston burette) connected to an

* To whom correspondence should be addressed

0032-3861/94/020360–07

Olivetti M20 computer. Titrations were made automatically by the addition of standard 0.1 M NaOH to a solution of the amino compound in the protonated form. The titration data were stored on a floppy disk and the basicity constant values evaluated by the Superquad program[12], on an Olivetti M28 computer. *Table 1* summarizes the experimental details of the potentiometric measurements.

Intrinsic viscosities were measured at 30°C with an Ubbelohde viscometer connected to an automatic Schott-Gerate AVS 310 timer.

Cyclic voltammetry measurements

Cyclic voltammetry (c.v.) was performed at ambient temperature in a nitrogen atmosphere with a BAS 100A multipurpose voltammeter in acetonitrile and dimethylsulfoxide (DMSO) containing 0.1 M tetrabutylammonium perchlorate as supporting electrolyte[13]. Platinum electrodes were used for the working and counter-electrodes, together with a saturated aqueous calomel electrode.

Synthesis of N-*lipoyl-1,3-diaminopropane* [*1*]

α-Lipoic acid (5.00 g, 24.2 mmol) was dissolved in anhydrous and alcohol-free chloroform (30 ml). Solid 1,1′-carbonyldiimidazole (5.00 g, 30.8 mmol) was added in small portions with stirring until bubbling ceased over 5 min. This solution was slowly added to a solution of 1,3-diaminopropane (8.79 g, 118.6 mmol) in alcohol-free $CHCl_3$ (20 ml) under stirring in an ice bath. Stirring was continued for 0.5 h in the cold and for 0.5 h at ambient temperature. The limpid yellow solution was washed with aqueous sodium chloride (10 wt%, 3 × 50 ml) and double-distilled water (3 × 50 ml). Then the solution was dried over sodium sulfate and the solvent removed under reduced pressure. The yield was 6.5 g (96%). Analysis: C, 47.4%; H, 7.9%; N, 9.6%. $C_{11}H_{22}N_2OS_2 \cdot H_2O$ requires: C, 47.1%; H, 8.6%; N, 10.0%.

Synthesis of 4-lipoylpiperazine [*2*]

α-Lipoic acid (5.00 g, 24.2 mmol) was dissolved in anhydrous and alcohol-free $CHCl_3$ (40 ml). Solid 1,1′-carbonyldiimidazole (5.00 g, 30.8 mmol) was added in small portions until bubbling ceased under stirring. This solution was slowly added to a solution of anhydrous piperazine (10.4 g, 120.7 mmol) dissolved in the same solvent $CHCl_3$ (30 ml) under stirring and cooling. The ice bath was maintained for 10 min and then the solution was kept at ambient temperature for 1 h. The yellow solution was washed with aqueous sodium chloride (10 wt%, 4 × 40 ml) and double-distilled water (3 × 50 ml). Then it was dried (Na_2SO_4) and the solvent removed under reduced pressure. The yield was 5.3 g (75%). Analysis: C, 49.8%; H, 7.7%; N, 9.5%. $C_{12}H_{22}N_2OS_2 \cdot H_2O$ requires: C, 49.3%; H, 8.3%; N, 9.6%.

Synthesis of poly(1-acryloyl-4-lipoylpiperazine)

The limpid yellow solution (10 wt%) of 1-acryloyl-4-lipoylpiperazine and azobisisobutyronitrile (AIBN) (0.1 mol%) in 1,4-dioxane was purged with nitrogen; the reaction mixture was allowed to react at 60°C for 24 h while the polymer precipitated out.

The monomer 1-acryloyl-4-lipoylpiperazine was obtained by dropwise addition of acryloyl chloride (0.01 mol) to compound **2** (0.01 mol) in anhydrous chloroform and in the presence of triethylamine. The temperature was maintained at 0°C for 15 min and then raised to ambient temperature over 1 h. The solution was washed with water, HCl (1 M), water, aqueous $NaHCO_3$ (10 wt%), water and finally dried (Na_2SO_4). Analysis: C, 53.9%; H, 7.3%; N, 8.1%. $C_{15}H_{24}N_2O_2S_2 \cdot 0.25H_2O$ requires: C, 54.1%; H, 7.4%; N, 8.4%.

Synthesis of copolymer (*poly*(*ABT*-co-*VPy*))

The monomer solution, which consisted of *N*-acryloylbenzotriazole (ABT) (0.858 g, 0.0050 mol), *N*-vinylpyrrolidinone (VPy) (1.15 g, 0.010 mol) and 1,4-dioxane (7 ml), was deoxygenated and the reaction initiated with AIBN (15 mg). The mixture was thermostatted at 70°C in an oil bath and polymerization was allowed to proceed to completion in 24 h, under nitrogen. The copolymer was precipitated in diethyl ether (100 ml) and the white powder recovered was washed with the same solvent. Yield (dry weight) was 1.88 g. Intrinsic viscosity $[\eta] = 0.16$ dl g^{-1} (in chloroform at 30°C).

Exchange reactions

A mixture of copolymer (0.50 g, 43 wt% ABT residues) and triethylamine (2 mol), dissolved in anhydrous chloroform (10 ml), was added to a $CHCl_3$ solution containing a two-fold excess of **1** (0.88 g, amino group content 75 wt%). The mixture was left to react in the cold (ice bath) with stirring for 1 h. Then it was maintained at ambient temperature overnight. The copolymer was precipitated in n-hexane (100 ml) and washed with hot $CHCl_3$ (40 ml) under reflux. The residue was a pale yellow powder, soluble only in hot DMSO. Yield was 0.80 g. Intrinsic viscosity $[\eta] = 0.14$ dl g^{-1} (in DMSO at 30°C).

Exchange reactions of poly(1-acryloylbenzotriazole) (poly(ABT), $[\eta] = 1.02$ dl g^{-1}) with compounds **1** and **2** were performed in DMSO (25 ml) at molar ratios 1:1 (0.68 g of **2**, amino group content 93 wt%, 2.30 mmol; 0.40 g poly(ABT), 2.30 mmol) and 1:1.5 (1.52 g of **1**, amino group content 75 wt%, 4.34 mmol; 0.52 g poly(ABT), 3.00 mmol), respectively. The solution was allowed to react in the presence of triethylamine at ambient temperature for 24 h. In all cases, the solid product was isolated by pouring the reaction mixture into an excess of acetone. The dried fine powder yielded 0.54 g

Table 1 Experimental details of potentiometric measurements[a] in 0.1 M NaCl at 25°C

Compound	$T_L \times 10^3$ (mol)	$T_{H^+} \times 10^3$ (mol)	C_T (mol dm^{-3})	pH range	Points
1	0.1677	0.4540	−0.1193	8.39–10.21	39
	0.2731	0.0000	0.1138	10.28–6.28	25
2	0.2966	0.5016	−0.1484	5.71–8.29	18
	0.2593	0.4552	−0.1484	7.66–10.02	31

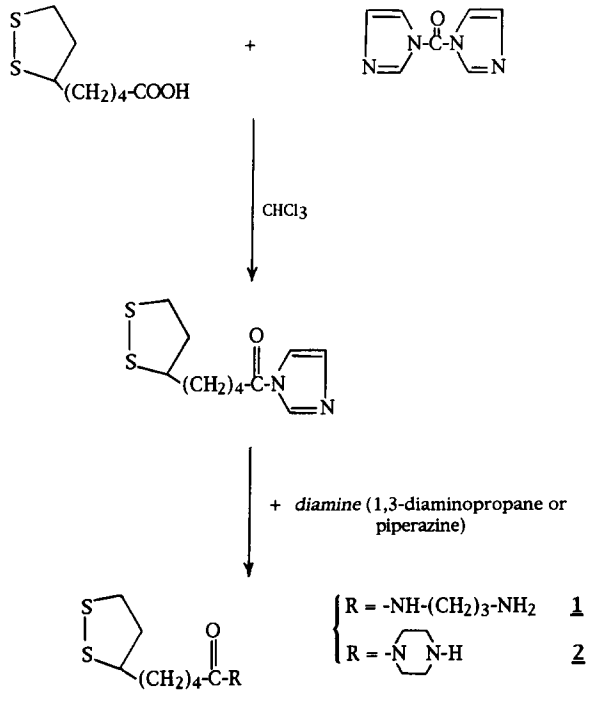
[a] T_L = initial amount of ligand; T_{H^+} = initial amount of hydrogen ions; C_T = titrant concentration (negative values refers to NaOH solution)

for the substitution of **2**, and 0.93 g for that of **1**. Analysis (derived from **2**): C, 53.9%; H, 6.0%; N, 10.9%. Analysis (derived from **1**): C, 48.7%; H, 7.1%; N, 7.9%. $(C_{14}H_{24}N_2O_2S_2 \cdot 1.5H_2O)_x$ requires: C, 48.9%; H, 7.9%; N, 8.1%.

RESULTS AND DISCUSSION

Low-molecular-weight compounds

Synthesis and structures. The two compounds **1** and **2**, containing the cyclic disulfide and the free amino group, were prepared with a fair yield in two reaction steps (*Scheme 1*). First, the imidazolide was prepared by addition of 1,1'-carbonyldiimidazole to α-lipoic acid, in anhydrous and alcohol-free chloroform. The solution of imidazolide was poured into a large excess of bis-primary (1,3-diaminopropane) or bis-secondary (piperazine) amine. The aminolipoyl derivative obtained was a bright orange, rubbery solid. The solid product was not soluble in chloroform at ambient temperature, but was soluble in hot $CHCl_3$ and some other organic solvents (acetonitrile, dimethylsulfoxide). The structure of the product was characterized by elemental analysis, infra-red and ^1H n.m.r. spectroscopy. Elemental analysis revealed a residual water molecule. This may be related to the presence of hydrophilic components, such as amido and primary or secondary amino groups. The formation of the amidic linkage was revealed by infra-red analysis. *Figure 1* shows the *FT*i.r. spectra of the two compounds. Compound **1** showed two characteristic frequencies for the amido group: amide I at 1640 cm^{-1} and amide II at 1550 cm^{-1}. Only the amide I at 1630 cm^{-1} was found in compound **2** due to the presence of the piperazine ring. Proton n.m.r. spectra agreed with the proposed structure. *Figure 2* shows the ^1H n.m.r. of compound **1** in DMSO-d_6. The chemical shifts for both compounds are reported in *Table 2* together with that of simple lipoic acid, by way of comparison.



Scheme 1

Physicochemical properties. The electrochemical and thermodynamic (basicity constants) properties of the two synthetic compounds were evaluated in solution. The basicity constant for the protonation of the free amino group was evaluated in 0.1 M NaCl at 25°C from potentiometric data. Titrations were performed with the addition of standard 0.1 M sodium hydroxide to a solution of ionized amino compound in the presence of a large excess of hydrochloric acid. Sharp end-points of the potentiometric titration curves allowed reliable determination of the free basic nitrogens present in both compounds. The solution became cloudy when the amino group reached a completely uncharged state, because the free compound is insoluble in water. Amino group

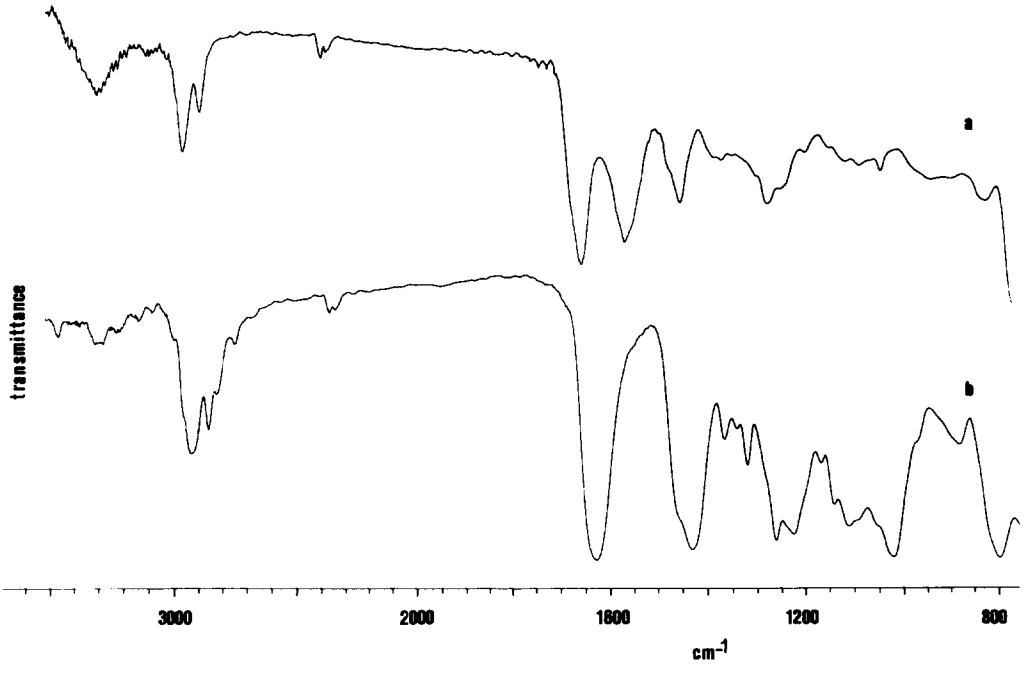


Figure 1 A.t.r./*FT*i.r. of (a) compound **1** and (b) compound **2**

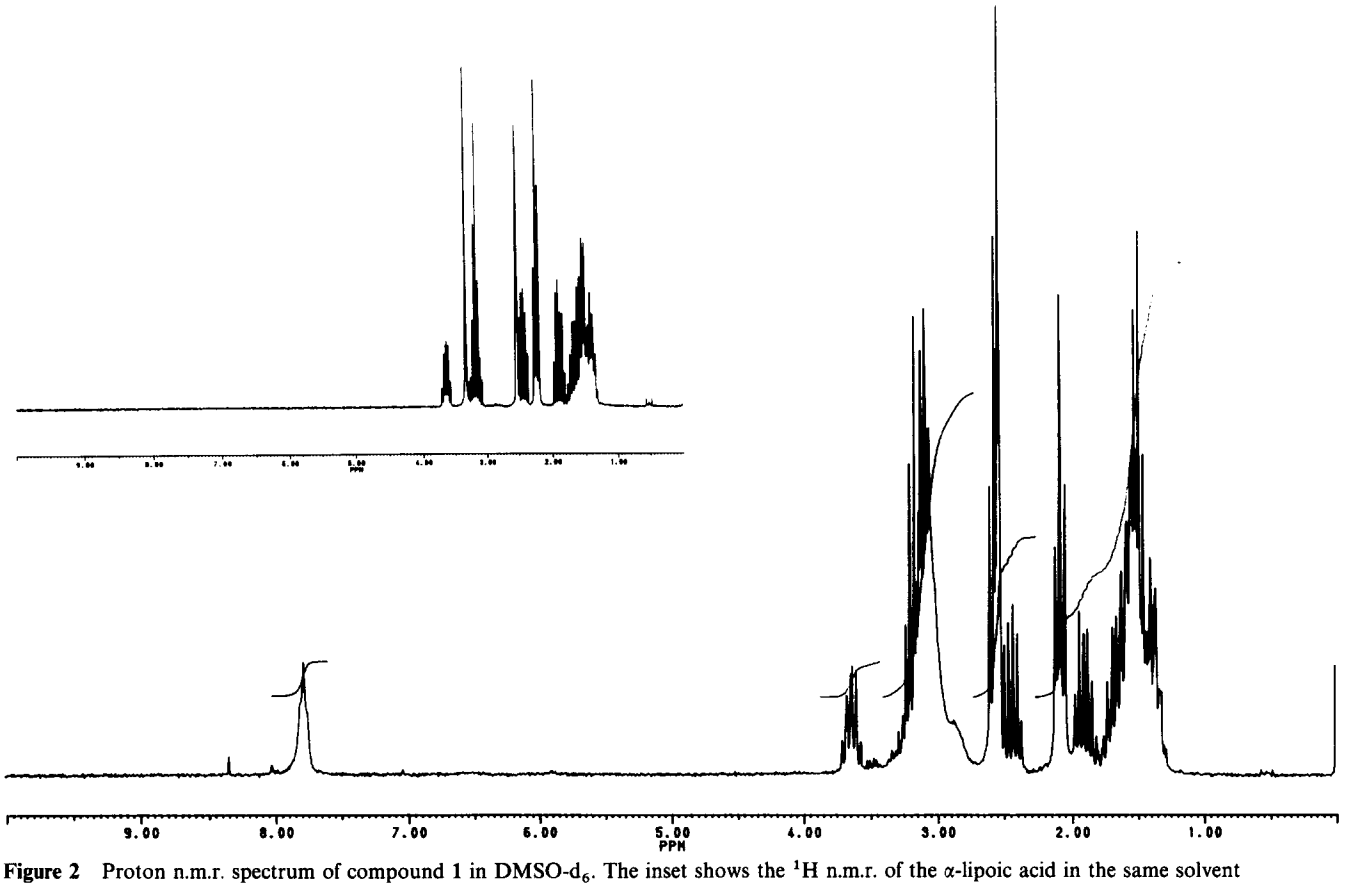


Figure 2 Proton n.m.r. spectrum of compound 1 in DMSO-d_6. The inset shows the ^{1}H n.m.r. of the α-lipoic acid in the same solvent

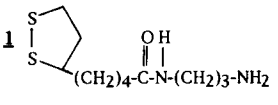
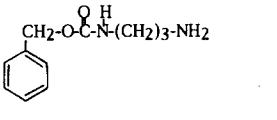
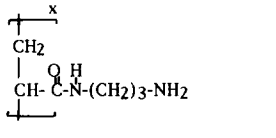
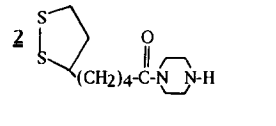
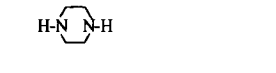
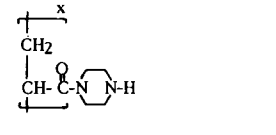
Table 2 Proton n.m.r. chemical shifts (DMSO-d_6/TMS) of low-molecular-weight compounds

R = -C(=O)-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH(S—S-CH$_2$-CH$_2$)

G F E D C B A

Structure	δ, J (Hz)
R-OH *H*	*Lipoic acid* 12 (s, 1H; *H*); 3.72–3.56 (m, 1H; *C*); 3.37–3.06 (m, 2H; *F*); 2.44 (q, 2H, $J=7$; *E*); 2.24 (t, 2H, $J=10$; *G*); 2.00–1.79 (m, 2H; *D*); 1.79–1.30 (m, 4H; *A*, *B*)
NH$_2$ *N* CH$_2$ *M* CH$_2$ *L* CH$_2$ *I* NH *H* R	*Compound* **1** 7.93–7.75br (m, 2H; *N*, *H*); 3.74–3.55 (m, 1H; *C*); 3.30–2.90 (m, 8H; *I*, *L*, *M*, *F*); 2.50–2.34 (m, 2H; *E*); 2.19 (t, 2H, $J=10$; *G*); 2.00–1.82 (m, 2H; *D*); 1.80–1.30 (m, 4H; *A*, *B*)
H *N* *I* CH$_2$ CH$_2$ *L* *H* CH$_2$ CH$_2$ *M* R	*Compound* **2** 3.72–3.55 (m, 9H; *I*, *H*, *L*, *M*, *C*); 3.30–3.10 (m, 2H; *F*); 2.86br (s, 1H; *N*); 2.75–2.59 (m, 2H; *E*); 2.60 (t, 2H, $J=10$; *G*); 2.10–1.80 (m, 2H; *D*); 1.79–1.31 (m, 4H; *A*, *B*)
P H, H *X* C=C *Q* H, C=O *I* CH$_2$ CH$_2$ *L* *H* CH$_2$ CH$_2$ *M* R	*1-Acryloyl-4-lipoylpiperazine* 6.83 (q, 1H, $J_{QX}=18$, $J_{PX}=12$; *X*); 6.20–5.65 (2q, 2H, $J_{PQ}=4$; *P*, *Q*); 3.74–3.40 (m, 9H; *H*, *I*, *L*, *M*, *C*); 3.25–3.09 (m, 2H; *F*); 2.55–2.40 (m, 2H; *E*); 2.36 (t, 2H, $J=9$; *G*); 2.00–1.80 (m, 2H; *D*); 1.80–1.35 (m, 4H; *A*, *B*)

Table 3 Basicity of monoamidated diamines at 25°C in 0.1 M NaCl

Compound	Log *K*	Ref.
1 	9.571(10)[b]	This paper
H_2N-$(CH_2)_3$-NH_2	10.52 8.74	14
	9.65	16
	9.31[a]	10
2 	7.77(6)[b]	This paper
	9.71 5.59	14
	7.13[a]	17

[a] Calculated at a degree of protonation $\alpha=0.5$
[b] Values in parentheses are standard deviations

content was 75% and 93% respectively for compounds **1** and **2**. The basicity constants (log K) are reported in *Table 3*, together with those of low-molecular-weight and polymeric analogues, for comparison. In both cases, compounds **1** and **2** showed only a single log K value. Its magnitude was lower than $\log K_1$ and higher than $\log K_2$ of the corresponding simple diamines (1,3-diaminopropane and piperazine)[14]. This depends on the inductive effects of the neighbouring amido group in monoamidated compounds **1** and **2**. In the case of compound **1**, this effect can be compared with the purposely synthesized benzyloxycarbonyl-1,3-propanediamine[15], which shows similar log K values[16]. Further comparison can be made with previously studied vinyl polymers carrying the simple diamine condensed at one end[10,17]. The uncharged polymer, at zero protonation, shows a log K value close to that of the corresponding low-molecular-weight compound. This fact strongly supports the validity of comparing polyelectrolytes and low-molecular-weight compounds with amino functional groups, as found for vinyl polymers carrying carboxyl groups[18].

The electrochemical behaviour in dimethylsulfoxide of compounds **1** and **2** showed a cyclic voltammetric (c.v.) response at a platinum electrode (*Figure 3*). Diagnostic criteria based on the c.v. responses revealed that the redox process is not reversible. Compound **2** exhibited only an anodic oxidation process ($E_a = 1.00$ V) unassociated with the oxidation process in the reverse scan. Similar irreversible behaviour was observed for compound **1**, which showed a single oxidation ($E_a = 1.07$ V) peak (*Table 4*). Compound **1** also showed a weak cathodic response in acetonitrile.

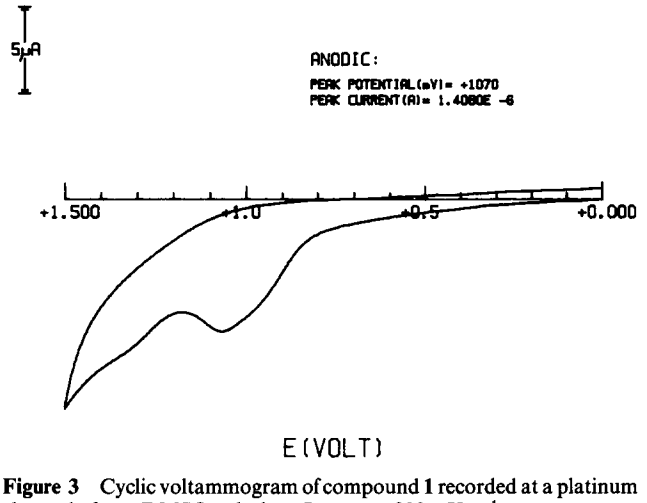


Figure 3 Cyclic voltammogram of compound **1** recorded at a platinum electrode for a DMSO solution. Scan rate 200 mV s^{-1}

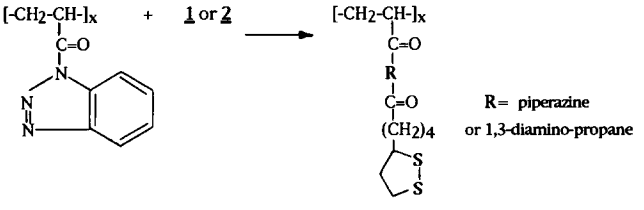
Table 4 Redox potentials of low-molecular-weight and polymeric compounds (Pt electrode vs. SCE)

Compound	Solvent	Voltage (mV) E_a	Voltage (mV) E_c	Sweep rate (mV s^{-1})
1	DMSO	1070	–	200
	CH_3CN	–	−1400	200
Copolymer with **1**	DMSO	1214	–	200
		1238	–	100
2	DMSO	1004	–	200
2/Cu^{2+}	DMSO[a]	550	–	200

[a] Complex species are present in DMSO with $\lambda_{max} = 680$ nm (14.7×10^3 cm^{-1})

Polymers

Exchange reactions of N-*alkylbenzotriazole in homo- and copolymers with compounds 1 and 2.* The ability of poly(*N*-alkylbenzotriazole) to enter into exchange reaction with the monoamidated compound was investigated by treating DMSO solutions of a synthesized polymer sample with amino compounds **1** and **2** at ABT/amine molar ratios ranging from 1:1 to 2:1, according to:



The extent of the exchange reaction was checked by nitrogen analysis and *FT*i.r. spectroscopy. In the latter case, the disappearance of the bands at 1730 cm^{-1} (attributed to the benzotriazolide C=O) and 770 cm^{-1} (attributed to substituted benzotriazole) was mainly considered[8]. With a molar ratio close to 1, the reaction of poly(*N*-alkylbenzotriazole) and compound **2** did not seem to be quantitative. The nitrogen content was found to be higher than the calculated value (*Table 5*). Examination of the *FT*i.r. spectra also revealed a limited exchange reaction. Comparison with the infra-red spectra of an authentic sample of the same polymer obtained by a direct route, i.e. by polymerization of 1-acryloyl-4-lipoylpiperazine (*Table 2*), showed small differences due to bands in the region mentioned above. However, a very strong and broad band appeared at 1640 cm^{-1} in the spectrum of both samples. This may clearly be attributed to the amide I band and suggests that the benzotriazole residue is substituted with the simple co-reactant **2**. The strong band at 1015 cm^{-1} due to the piperazine ring was further evidence of substitution. The nitrogen content agreed well when the molar ratio of simple compound **1** with respect to ABT residues was increased to 1.5:1 (*Table 5*). In all cases, however, the polymers obtained were insoluble in organic solvents. To obtain a more soluble polymer, we introduced the *N*-vinylpyrrolidinone unit into a copolymer with acryloylbenzotriazole:

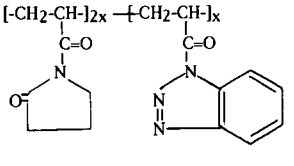


Table 5 Exchange reactions of *N*-acryloylbenzotriazole in poly(ABT) with monoamidated compounds **1** and **2**

Starting polymer	Amino compound	Amino/ABT molar ratio	N content (%) Calcd for 100% exchange	N content (%) Found
poly(ABT)	**2**	1:1	8.53	10.97
	1	1.5:1	8.15[a]	7.90

[a] Calculated for $C_{14}H_{24}N_2O_2S_2 \cdot 1.5H_2O$

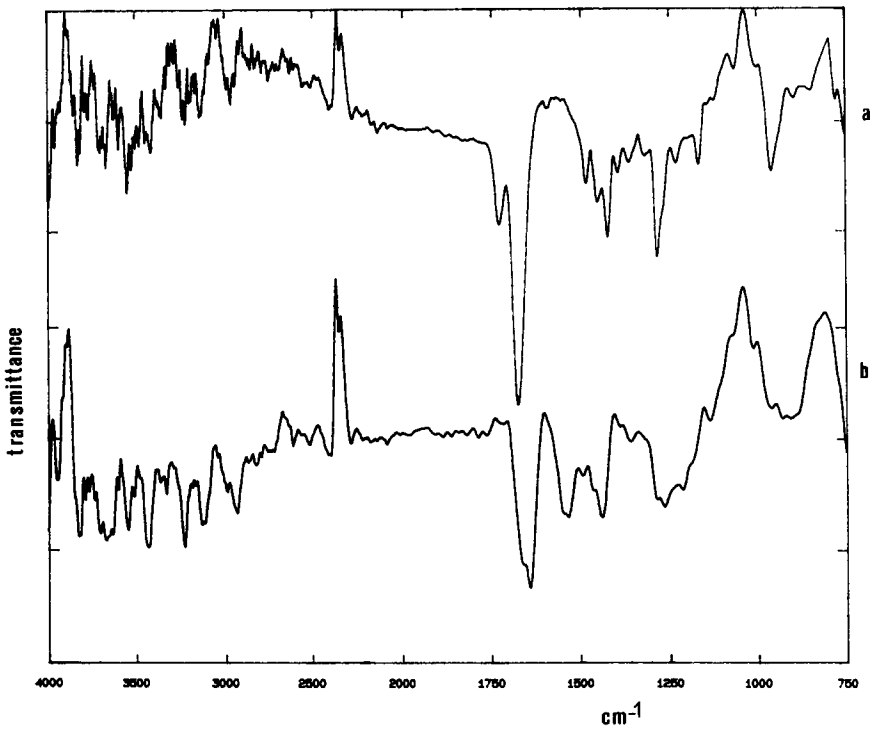


Figure 4 *FT*i.r. spectra of the copolymer (ABT-*co*-VPy) before (a) and after (b) the exchange reaction with the compound **1**

The ABT residue was exchanged with compound **1** in a 2:1 molar ratio. Under these conditions, the reaction was substantially quantitative. This was confirmed by i.r. spectra (*Figure 4*), which showed the complete absence of substituted benzotriazole. Furthermore, the amide I band was very strong at 1645 cm^{-1} and there were two close strong bands at 1555 and 1540 cm^{-1}. The last two are amide II bands and can probably be attributed to the two amido groups in the lateral chain of the vinyl copolymer. The copolymer, even carrying substituted disulfide ring, was soluble in DMSO owing to the vinylpyrrolidinone units, and the cyclic voltammetric responses at a platinum electrode were recorded in this solvent. Once more the characteristic single oxidation process, without a directly associated response in the reverse scan, was observed in the copolymer carrying the disulfide ring. The cyclic voltammograms thus consist of a single redox peak having an anode potential that slowly changes with scan rates (*Table 4*). The cyclic voltammogram is essentially identical to that of the corresponding simple monoamidated compounds except that the oxidation potential is shifted to higher values, increasing with decreasing scan rate. The higher oxidation potential of the anode peak of the copolymer is probably due to electronic and steric effects of the macromolecular chain, absent in simple compound **1**. The amino group in **1** has more electron-withdrawing properties than the amido group in the copolymer. This point needs more detailed study to clarify the mechanism of the redox processes.

CONCLUSIONS

The synthesis of monoamidated compounds using carbonyldiimidazole is a convenient way to form lipoamide–amines that are useful for binding to various polymeric matrices[4].

The exchange reaction with the benzotriazole residue in vinyl polymers allows easy introduction of the cyclic disulfide. The latter can be reduced to a dihydro-type polymer having a powerful reducing character. The reaction can be performed better if the original polymer is in a soluble form, as in the case of copolymers with *N*-vinylpyrrolidinone units.

Electrochemical data on synthetic compounds carrying the cyclic disulfide only showed an anode response in cyclic voltammetry, and were also irreversible. The anode peak potential increased on going from the simple low-molecular-weight compounds to the copolymer, while the presence of copper(II) ions led to a sharp drop in the voltage as the simple compounds formed complex species in dimethylsulfoxide (*Table 4*). The clarification of this peculiar behaviour calls for further study.

ACKNOWLEDGEMENTS

This work was supported by a grant to the International Joint Research Project from NEDO, Japan. One of us (M. C.) wishes to thank Professor P. Ferruti (Brescia University) for his valuable suggestions for the synthesis. Thanks are due to Professor A. Cinquantini (Siena University) for recording the voltammograms.

REFERENCES

1 Ise, N. and Tabushi, I. 'An Introduction to Speciality Polymers', Cambridge University Press, Cambridge, 1983
2 Casolaro, M. and Ito, Y. 'The Development of Science for the Improvement of Human Life', 1st Kyoto–Siena Symp. (Eds. F. Casprini and R. Barbucci), 1992
3 Nambu, Y., Acar, M. H., Suzuki, T. and Endo, T. *Makromol. Chem.* 1988, **189**, 495
4 Gorecki, M. and Patchornik, A. *Biochim. Biophys. Acta* 1973, **303**, 36
5 Nambu, Y., Kijima, M. and Endo, T. *Macromolecules* 1987, **20**, 962

6 Suzuki, T., Nambu, Y. and Endo, T. *Macromolecules* 1990, **23**, 1579
7 Ferruti, P., Feré, A. and Cottica, G. *J. Polym. Sci., Polym. Chem. Edn.* 1974, **12**, 553
8 Ferruti, P., Vaccaroni, F. and Tanzi, M. C. *J. Polym. Sci., Polym. Chem. Edn.* 1978, **16**, 1435
9 Ferruti, P., Tanzi, M. C., Rusconi, L. and Cecchi, R. *Makromol. Chem.* 1981, **182**, 2183
10 Barbucci, R., Casolaro, M., Nocentini, M., Reginato, G. and Ferruti, P. *Makromol. Chem.* 1986, **187**, 1953
11 Barbucci, R., Casolaro, M., Danzo, N., Barone, V., Ferruti, P. and Angeloni, A. *Macromolecules* 1983, **16**, 456
12 Gans, P., Sabatini, A. and Vacca, A. *J. Chem. Soc., Dalton Trans.* 1985, 1195
13 Zanello, P., Cinquantini, A., Ghilardi, C. A., Midollini, S., Moneti, S., Orlandini, A. and Bencini, A. *J. Chem. Soc., Dalton Trans.* 1990, 3761
14 Smith, R. M. and Martell, A. E. 'Critical Stability Constants', Plenum Press, New York, 1975
15 Lawson, W. B., Leafer, Jr, M. D., Tewes, A. and Rao, G. J. S. *Hoppe-Seyler's Z. Physiol. Chem.* 1968, **349**, 251
16 Casolaro, M. Unpublished data
17 Barbucci, R., Casolaro, M., Ferruti, P., Tanzi, M. C., Grassi, L. and Barozzi, C. *Makromol. Chem.* 1984, **185**, 1525
18 Barbucci, R., Casolaro, M. and Magnani, A. *Coord. Chem. Rev.* 1992, **120**, 29