Sulfur-containing optically active polymers: 2. Synthesis and chiroptical properties of poly(γ-ketosulfide)s containing the (2*R*,3*R*)-1,4-dimercapto-2,3-butanediolbutyraldehyde-acetal moiety

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(Received 6 August 1992; revised 9 December 1992)

Optically active poly(γ-ketosulfide)s containing the (2*R*,3*R*)-1,4-dimercapto-2,3-butanediol moiety were reacted with butyraldehyde to obtain the corresponding acetalized derivatives. The optically active low-molecular-weight analogues were also similarly prepared. High- and low-molecular-weight products were characterized by spectroscopic methods and chiroptical techniques. The conformational and stereochemical features of the macromolecules, as compared with the polymeric precursors as well as the low-molecular-weight analogues, are discussed on the basis of nuclear magnetic resonance (n.m.r.) and circular dichroism measurements. In particular, n.m.r. data indicate that the acetalization reaction does not appreciably modify the diastereomeric distribution of the constitutional repeating units and circular dichroism spectra confirm the presence of asymmetric induction on the chromophoric groups, although no evidence is found of structurally ordered conformations having one largely prevailing single chirality.

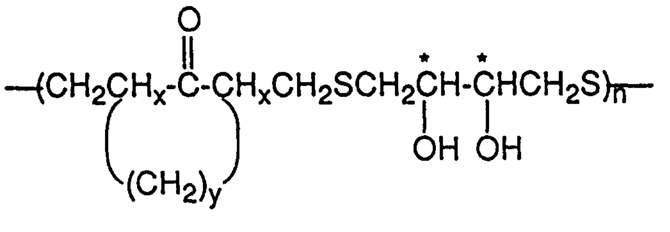
(Keywords: optically active poly(γ-ketosulfide)s; (−)-L-dithiothreitol; induced optical activity)

INTRODUCTION

In a previous paper[1] we reported the synthesis and characterization of optically active poly(γ-ketosulfide)s derived by reaction of the bis-Mannich base of acetone [1,3-bis(dimethylaminomethyl)-2-propanone, BBA] or cyclohexanone [2,6-bis(dimethylaminomethyl)cyclohexanone, BBC] with (−)(2*R*,3*R*)-1,4-dimercapto-2,3-butanediol, otherwise named L-dithiothreitol (DTT), or by polyaddition of the same dithiol to $\alpha, \beta, \alpha', \beta'$-unsaturated ketones, such as dibenzalacetone (1,5-diphenyl-1,4-pentadien-3-one, DBA) or dibenzalcyclohexanone (2,6-dibenzylidenecyclohexanone, DBC). By these routes the corresponding optically active polymeric derivatives poly(BBA-DTT) **1**, poly(BBC-DTT) **2** as well as poly(DBA-DTT) **3** and poly(DBC-DTT) **4**, respectively, have been obtained.

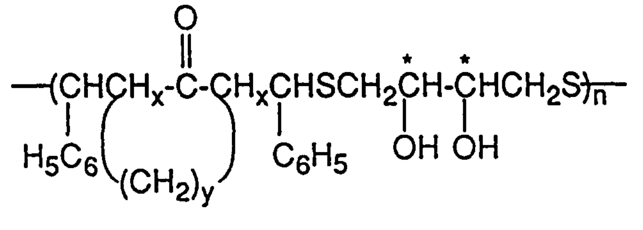
The above reactions proceed readily yielding products having number-average molecular weights ($\bar{M}_n$) and diastereomeric contents of repeating units similar to previously synthesized analogous poly(γ-ketosulfide)s[2,3]. However, the low solubility of some of them prevented their complete characterization. In particular, for polymers **1** and **2**, no information on their conformational features in solution could be drawn from circular dichroism (c.d.) and optical activity measurements.

In order to overcome this difficulty, we have carried out the functionalization of all the above polymers by allowing them to react with butyraldehyde (BA), so as to obtain the corresponding soluble acetalized derivatives poly(BBA-DTT)-BA **5**, poly(BBC-DTT)-BA **6**, poly(DBA-DTT)-BA **7** and poly(DBC-DTT)-BA **8** (*Scheme 1*), in which the configuration of chiral centres,



x = 2 ; y = 0 : poly(BBA-DTT) **1**

x = 1 ; y = 3 : poly(BBC-DTT) **2**



x = 2 ; y = 0 : poly(DBA-DTT) **3**

x = 1 ; y = 3 : poly(DBC-DTT) **4**

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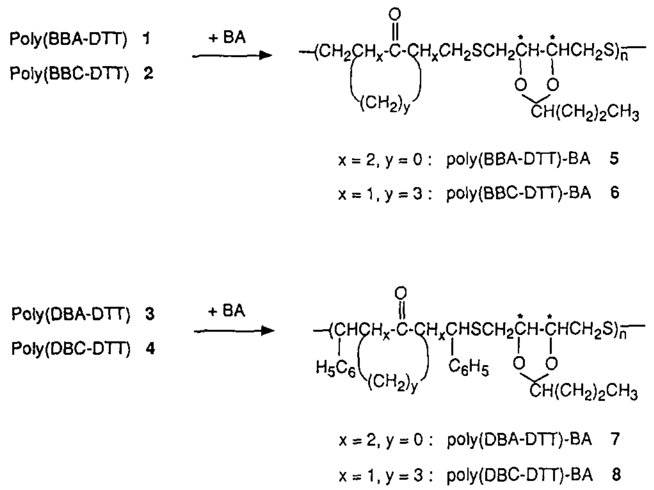
not involved in the reaction, is the same as in the polymeric precursors, but the conformational rigidity of the macromolecules should be modified, owing to both the formation of cyclic structures along the polymer backbone and the disappearance of groups capable of giving rise to inter- or intramolecular hydrogen bonding.

Moreover, for comparison with the macromolecular derivatives, the optically active low-molecular-weight compounds (MVK-DTT)-BA **9** and (MMC-DTT)-BA **10** have been prepared from butyraldehyde and the previously described[1] precursors (−)(2*R*,3*R*)-1,4-bis(3-oxobutylthio)-2,3-butanediol (MVK-DTT) and (−)(2*R*,3*R*)-1,4-bis(2-oxocyclohexylmethylthio)-2,3-butanediol (MMC-DTT) (*Scheme 2*).

Analogously, (MBA-DTT)-BA **11** and (MBC-DTT)-BA **12** have been synthesized from (−)(2*R*,3*R*)-1,4-bis(3-oxo-1-phenylbutylthio)-2,3-butanediol (MBA-DTT)[1] and (−)(2*R*,3*R*)-1,4-bis[2-(oxocyclohexyl)phenylmethylthio]-2,3-butanediol (MBC-DTT)[1], respectively (*Scheme 3*).



x = 2, y = 0 : poly(BBA-DTT)-BA **5**

x = 1, y = 3 : poly(BBC-DTT)-BA **6**

x = 2, y = 0 : poly(DBA-DTT)-BA **7**

x = 1, y = 3 : poly(DBC-DTT)-BA **8**

Scheme 1

EXPERIMENTAL

Starting materials

The synthesis and characterization of polymeric precursors **1**–**4** and low-molecular-weight analogues have been described in the preceding part[1] of this series. The butyraldehyde (Aldrich) employed for acetalization reactions was purified by distillation just before use.

Physicochemical measurements

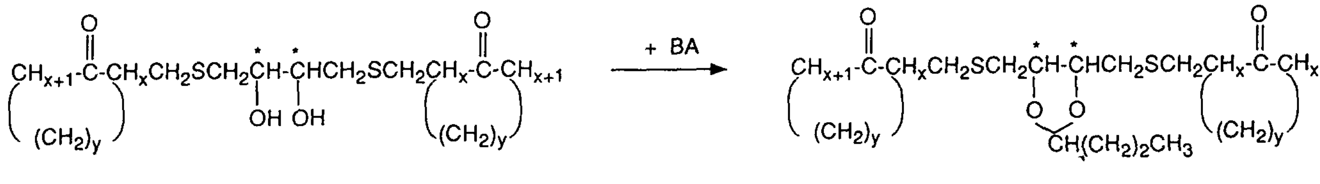
Fourier transform infra-red (*FT*i.r.) spectra were recorded on a Perkin–Elmer model 1750 spectrophotometer equipped with a Perkin–Elmer model 7700 data station. The samples were prepared as KBr pellets or liquid films on KBr discs.

Number-average molecular weights were determined using a Knauer 11 vapour pressure osmometer with $CHCl_3$ as solvent at 37°C. Intrinsic viscosities were measured in $CHCl_3$ at 30°C using an Ubbelohde dilution viscometer.

^1H- and ^{13}C-n.m.r. spectra were performed at 200 and 50.3 MHz, respectively, using a Varian FT-NMR Gemini 200 spectrometer on samples in $CDCl_3$ solution. Chemical shifts are given in δ (ppm) using tetramethylsilane (TMS) as internal standard.

Elemental analyses were carried out on a Carlo Erba CHN/S elemental analyser model 1106.

U.v. absorption spectra were recorded using a Jasco UVIDEC-510 spectrophotometer on samples in $CHCl_3$ solution at concentrations between about 4×10^{-3} and $5\times10^{-3}\,mol\,l^{-1}$ (in terms of repeating units for the polymers) by using cell path lengths of 1 and 0.1 cm for the 350–250 and 250–230 nm spectral regions, respectively. C.d. spectra were performed on a Jasco J-500A dichrograph using the same cell path lengths, solvent and sample concentrations as for u.v. measurements in the corresponding spectral regions; molar (decadic) absorption coefficients ε and $\Delta\varepsilon$ are expressed in $l\,mol^{-1}\,cm^{-1}$.



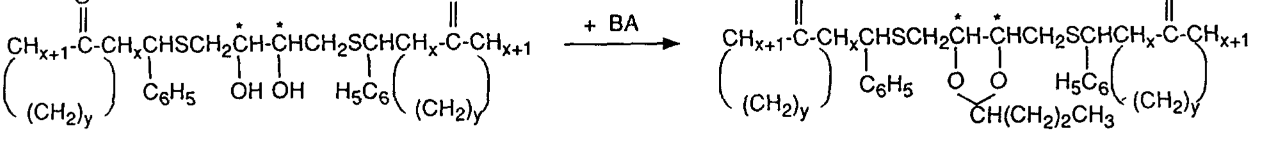
x = 2 , y = 0 : MVK-DTT

x = 1 , y = 3 : MMC-DTT

x = 2 , y = 0 : (MVK-DTT)-BA **9**

x = 1 , y = 3 : (MMC-DTT)-BA **10**

Scheme 2



x = 2 , y = 0 : MBA-DTT

x = 1 , y = 3 : MBC-DTT

x = 2 , y = 0 : (MBA-DTT)-BA **11**

x = 1 , y = 3 : (MBC-DTT)-BA **12**

Scheme 3

Optical activity measurements were made using a Jasco DIP-360 polarimeter on $CHCl_3$ solutions at 25°C (concentration, $c = 1\ \mathrm{g\ dl^{-1}}$), using a cell path length of 1 dm.

Melting points were determined in glass capillaries with a Büchi 510 apparatus at a heating rate of $1^\circ\mathrm{C\ min^{-1}}$.

Polymers

*Acetalization of polymers **1–4** with butyraldehyde. General procedure* (*ref. 4*). Each polymer, suspended or dissolved in methylene dichloride in the presence of a fivefold molar excess of butyraldehyde and a catalytic trace of *p*-toluensulfonic acid, was refluxed until complete dissolution of the suspended material occurred (1.5–3 h). Part of the solvent was distilled off using a Dean–Stark apparatus to remove the small amount of water formed during the reaction. The crude final solution was then washed with dilute aqueous $NaHCO_3$, water and finally dried (Na_2SO_4). Polymers **5–8** were obtained by coagulation with excess methanol and purified by reprecipitation.

Poly(*BBA-DTT*)*-BA* ***5***. Yield 74%. *FT*i.r.: 1714 ($\nu_{C=O}$), 1108, 1504, 1022 (ν_{C-O} cyclic acetal) $\mathrm{cm^{-1}}$. ^1H n.m.r.: 5.05 (t, 1 H, O–CH–O), 3.97 (m, 2 H, $CH_2C\underline{H}C\underline{H}CH_2$), 2.94–2.58 (m, 12 H, CH_2S and CH_2CO), 1.63 and 1.42 (m, 4 H, $C\underline{H}_2C\underline{H}_2CH_3$), 0.95 (t, 3 H, CH_3). $[\alpha]_D = +9.9\ \mathrm{deg\ dm^{-1}\ g^{-1}\ cm^3}$. Elemental analysis: calculated for $(C_{13}H_{22}O_3S_2)_n$ $(290.4)_n$: C 53.76, H 7.64, S 22.08; found: C 54.01, H 7.80, S 21.75.

Poly(*BBC-DTT*)*-BA* ***6***. Yield 70%. *FT*i.r.: 1708 ($\nu_{C=O}$), 1107, 1055, 1021 (ν_{C-O} cyclic acetal) $\mathrm{cm^{-1}}$. ^1H n.m.r.: 5.02 (t, 1 H, O–CH–O), 3.91 (m, 2 H, $CH_2C\underline{H}C\underline{H}CH_2$), 3.12–2.24 (m, 10 H, CH_2S and CHCO), 1.92–1.11 (m, 10 H, cyclohexanone ring protons and $C\underline{H}_2C\underline{H}_2CH_3$), 0.93 (t, 3 H, CH_3). $[\alpha]_D = +9.7\ \mathrm{deg\ dm^{-1}\ g^{-1}\ cm^3}$. Elemental analysis: calculated for $(C_{16}H_{26}O_3S_2)_n$ $(330.5)_n$: C 58.15, H 7.93, S 19.40; found: C 57.91, H 7.74, S 19.02.

Poly(*DBA-DTT*)*-BA* ***7***. Yield 85%. *FT*i.r.: 3060, 3028 (ν_{CH} arom.), 1719 ($\nu_{C=O}$), 1105, 1053, 1022 (ν_{C-O} cyclic acetal), 757, 698 (subst. arom.) $\mathrm{cm^{-1}}$. ^1H n.m.r.: 7.25 (m, 10 H, arom.), 4.85 (m, 1 H, O–CH–O), 4.32 (m, 2 H, $C\underline{H}Ph$), 3.60 (m, 2 H, $CH_2C\underline{H}C\underline{H}CH_2$), 2.81 (m, 4 H, CH_2S), 2.33 (m, 4 H, CH_2CO), 1.64 and 1.32 (m, 4 H, $C\underline{H}_2C\underline{H}_2CH_3$), 0.88 (t, 3 H, CH_3). $[\alpha]_D = +1.2\ \mathrm{deg\ dm^{-1}\ g^{-1}\ cm^3}$. Elemental analysis: calculated for $(C_{25}H_{30}O_3S_2)_n$ $(442.6)_n$: C 67.84, H 6.83, S 14.49; found: C 68.06, H 6.98, S 14.10.

Poly(*DBC-DTT*)*-BA* ***8***. Yield 68%. *FT*i.r.: 3059, 3027 (ν_{CH} arom.), 1714 ($\nu_{C=O}$), 1107, 1077, 1020 (ν_{C-O} cyclic acetal), 744, 700 (subst. arom.) $\mathrm{cm^{-1}}$. ^1H n.m.r.: 7.25 (m, 10 H, arom.), 4.86 (m, 1 H, O–CH–O), 4.29 (m, 2 H, $C\underline{H}Ph$), 3.55 (m, 2 H, $CH_2C\underline{H}C\underline{H}CH_2$), 2.97–2.10 (m, 6 H, CH_2S and CHCO), 1.89–1.10 (m, 10 H, cyclohexanone ring protons and $C\underline{H}_2C\underline{H}_2CH_3$), 0.89 (t, 3 H, CH_3). $[\alpha]_D = -2.8\ \mathrm{deg\ dm^{-1}\ g^{-1}\ cm^3}$. Elemental analysis: calculated for $(C_{28}H_{34}O_3S_2)_n$ $(482.7)_n$: C 69.68, H 7.10, S 13.29; found: C 69.46, H 7.36, S 13.04.

Low-molecular-weight analogues

Acetalization of MVK-DTT, MMC-DTT, MBA-DTT and MBC-DTT with butyraldehyde. General procedure (*ref. 4*). Each low-molecular-weight substrate and a fivefold molar excess of butyraldehyde, dissolved in CH_2Cl_2 (~30 ml/0.5 mmol of substrate), in the presence of a catalytic trace of *p*-toluenesulfonic acid, were refluxed for 1 h until the expected amount of water formed in the process was distilled off. The reaction mixture was then washed with dilute $NaHCO_3$, dried (Na_2SO_4) and evaporated to dryness under reduced pressure. The obtained crude product was finally purified by column chromatography (SiO_2, eluent benzene followed by chloroform).

(+)(*2*R,*3*R)*-1,4-Bis*(*3-oxobutylthio*)*-2,3-butanediol-butyraldehydeacetal* (*MVK-DTT*)*-BA* ***9***. Yield 95%. *FT*i.r. (liquid film): 1715 ($\nu_{C=O}$), 1109, 1055, 1019 (ν_{C-O} cyclic acetal) $\mathrm{cm^{-1}}$. ^1H n.m.r.: 5.08 (t, 1 H, O–CH–O), 3.97 (m, 2 H, $CH_2C\underline{H}C\underline{H}CH_2$), 2.90–2.60 (m, 12 H, CH_2SCH_2 and CH_2CO), 2.18 (s, 6 H, CH_3CO), 1.70–1.55 and 1.50–1.30 (m, 4 H, $C\underline{H}_2C\underline{H}_2CH_3$), 0.92 (t, 3 H, $CH_2CH_2C\underline{H}_3$). ^{13}C n.m.r.: 207.11, 207.06 ($CH_3\underline{C}OCH_2$), 104.40 (OCHO), 81.31, 79.83 ($SCH_2\underline{C}H\underline{C}HCH_2S$), 43.79 ($CH_3CO\underline{C}H_2$), 36.40 ($CH\underline{C}H_2CH_2CH_3$), 35.28, 34.90 ($S\underline{C}H_2CHCH\underline{C}H_2S$), 26.63, 26.49 ($CH_3COCH_2\underline{C}H_2$), 17.28 ($CH_2\underline{C}H_2CH_3$), 14.11 ($CH_2CH_2\underline{C}H_3$). $[\alpha]_D = +9.9\ \mathrm{deg\ dm^{-1}\ g^{-1}\ cm^3}$. Elemental analysis: calculated for $C_{16}H_{28}O_4S_2$ (348.5): C 55.14, H 8.10, S 18.40; found: C 55.28, H 8.15, S 18.65.

(+)(*2*R,*3*R)*-1,4-Bis*(*2-oxocyclohexylmethylthio*)*-2,3-butanediol butyraldehydeacetal* (*MMC-DTT*)*-BA* ***10***. This compound, constituted by a diastereomeric mixture of isomers (92% yield), was submitted to a final purification by column chromatography (SiO_2, eluent benzene/chloroform 1:1 to 2:1 v/v). *FT*i.r. (liquid film): 1708 ($\nu_{C=O}$), 1111, 1056, 1021 (ν_{C-O} cyclic acetal) $\mathrm{cm^{-1}}$. ^1H n.m.r.: 5.02 (t, 1 H, O–CH–O), 3.93 (m, 2 H, $CH_2C\underline{H}C\underline{H}CH_2$), 3.05 and 2.98 (two t, 2 H, $C\underline{H}_XH_BS$ bonded at C-2 of cyclohexanone ring), 2.85–2.63 (m, 4 H, $SC\underline{H}_2CHO$), and 2.62–2.19 (m, 10 H, $CH_X\underline{H}_BS$ bonded at C-2 of cyclohexanone ring and CHCO, CH_2CO and $C\underline{H}_AH_B$ at positions 2, 6 and 3, respectively, of cyclohexanone ring), 2.15–1.32 (m, 14 H, $CH_A\underline{H}_B$ and CH_2 groups at positions 3, 4 and 5, respectively, of cyclohexanone ring and $C\underline{H}_2C\underline{H}_2CH_3$), 0.91 (t, 3 H, CH_3). ^{13}C n.m.r.: 211.90 (C=O), 104.39 (OCHO), 81.28, 79.92, 79.83 ($SCH_2\underline{C}H\underline{C}HCH_2S$), 51.39, 51.29 (CH at position 2 of cyclohexanone ring), 42.19 (CH_2 at position 6 of cyclohexanone ring), 36.45 ($CH\underline{C}H_2CH_2CH_3$), 36.05, 36.00, 35.71, 35.57 ($S\underline{C}H_2CHCH\underline{C}H_2S$), 33.72, 33.63 ($CH_2$ at position 3 of cyclohexanone ring), 32.79, 32.72 ($COCH\underline{C}H_2S$), 28.05 and 25.16 (CH_2 groups at positions 5 and 4, respectively, of cyclohexanone ring), 17.30 and 14.14 ($CHCH_2\underline{C}H_2CH_3$ and $CHCH_2CH_2\underline{C}H_3$, respectively). $[\alpha]_D = +9.2\ \mathrm{deg\ dm^{-1}\ g^{-1}\ cm^3}$. Elemental analysis: calculated for $C_{22}H_{36}O_4S_2$ (428.6): C 61.64, H 8.47, S 14.96; found: 61.47, H 8.61, S 14.73.

(−)(*2*R,*3*R)*-1,4-Bis*(*3-oxo-1-phenylbutylthio*)*-2,3-butanediol butyraldehydeacetal* (*MBA-DTT*)*-BA* ***11***. Yield 91%. *FT*i.r. (liquid film): 3061, 3029 (ν_{CH} arom.), 1718 ($\nu_{C=O}$), 1109, 1054, 1021 (ν_{C-O} cyclic acetal), 759, 700 (subst. arom.) $\mathrm{cm^{-1}}$. ^1H n.m.r.: 7.28 (m, 10 H, arom.), 4.91 (m, 1 H, O–CH–O), 4.40 (m, 2 H, $C\underline{H}$-Ph), 3.68 (m, 2H, $SCH_2C\underline{H}C\underline{H}CH_2S$), 2.91 (m, 4 H, CH_2S), 2.40 (m, 4 H, CH_2CO), 2.05 (two s, 6 H, CH_3CO), 1.57 and 1.39 (m, 2 H and 2 H, respectively, $C\underline{H}_2C\underline{H}_2CH_3$), 0.90 (t, 3 H, $CH_2CH_2C\underline{H}_3$). $[\alpha]_D = -4.4\ \mathrm{deg\ dm^{-1}\ g^{-1}\ cm^3}$.

Elemental analysis: calculated for $C_{28}H_{36}O_4S_2$ (500.7): C 67.16, H 7.25, S 12.81; found: C 66.85, H 7.44, S 12.63.

(−)(2R,3R)-*1,4-Bis[2-(oxocyclohexyl)phenylmethylthio]-2,3-butanediol butyraldehydeacetal (MBC-DTT)-BA **12***. Yield 95%. *FT*i.r. (liquid film): 3059, 3026 (ν_{CH} arom.), 1713 ($\nu_{C=O}$), 1112, 1073, 1021 (ν_{C-O} cyclic acetal), 758, 701 (subst. arom.) cm^{-1}. ^1H n.m.r.: 7.30 (m, 10 H, arom.), 4.90 (m, 1 H, O–CH–O), 4.42 (m, 2 H, $C\underline{H}$-Ph), 3.69 (m, 2H, $SCH_2C\underline{H}C\underline{H}CH_2S$), 2.97–2.10 (m, 10 H, CH_2S, CH and CH_2 at positions 2 and 6, respectively, of cyclohexanone ring), 2.10–1.15 (m, 16 H, CH_2 groups at positions 3, 4 and 5, respectively, of cyclohexanone ring and $C\underline{H}_2C\underline{H}_2CH_3$), 0.90 (t, 3 H, CH_3). $[\alpha]_D = -15.9$ deg dm^{-1} g^{-1} cm^3. Elemental analysis: calculated for $C_{34}H_{44}O_4S_2$ (580.8): C 70.30, H 7.64, S 11.04; found: C 70.05, H 7.53, S 11.15.

RESULTS AND DISCUSSION

The structures of the prepared polymers were confirmed by *FT*i.r. spectroscopy, n.m.r. spectrometry and elemental analysis (see Experimental). In particular, in polymers **5–8** all the relevant i.r. bands expected for ketonic and aromatic (when present) groups were exhibited and the presence of cyclic acetal bands combined with the simultaneous disappearance of hydroxyl bands related to the pristine polymers **1–4**[1] was observed. I.r. spectra of **5–8** are reported in *Figure 1*.

N.m.r. chemical shifts as well as the integrated areas of ^1H n.m.r. signals were also in agreement with the proposed structures, although a deeper investigation of the spectra was required in order to interpret correctly the multiplicity of signals connected with the creation of a dioxolane ring along the polymer backbone (see below).

Molecular weights of polymers **7** and **8** (*Table 1*), as compared with the corresponding values of the starting polymers **3** and **4**[1], indicated that no significant degradation occurred during the functionalization reaction. Assuming that the same holds for the acetalization of polymers **1** and **2**, their number-average molecular weights can be evaluated from the corresponding experimental data found for polymers **5** and **6**, respectively (*Table 1*). Intrinsic viscosity values (*Table 1*) appeared not to be substantially affected by acetalization of hydroxyl groups of DTT moieties (see **3** *versus* **7** and **4** *versus* **8**). These results seem to suggest that intramolecular hydrogen bonding in unacetalized polymers plays a major role. As a consequence, the hydrodynamic volume of the macromolecules does not appreciably change on functionalization. In other words, the solute/solvent interactions as well as the conformational situation of the macromolecules should remain substantially unchanged as a whole. In contrast, the introduction of phenyl groups along the polymer backbone appears to decrease viscosity (see **6** *versus* **8**), thus suggesting decreased interchain interactions. Finally, it is worth noting the relevant gain of solubility of the acetalized polymers as compared with the corresponding hydroxy derivatives (*Table 1*).

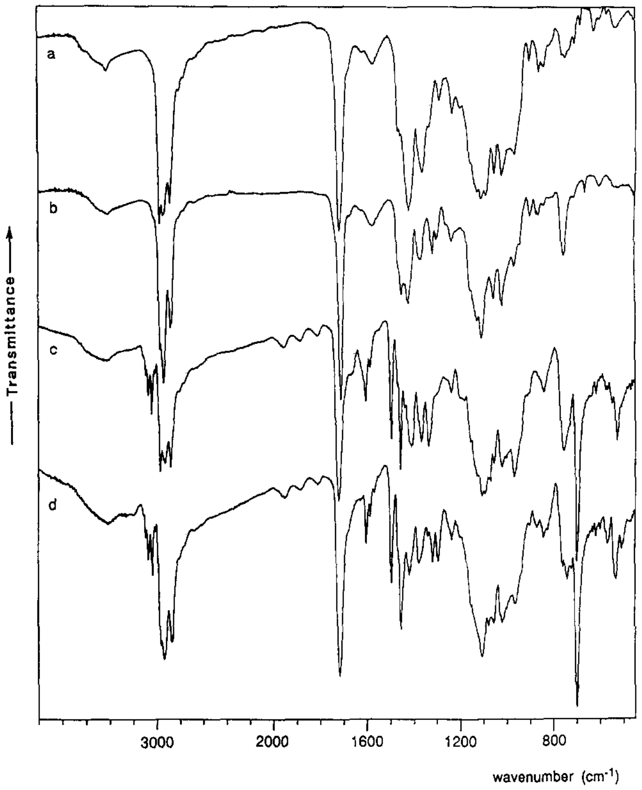


Figure 1 *FT*i.r. spectra of (a) poly(BBA-DTT)-BA (**5**), (b) poly(BBC-DTT)-BA (**6**), (c) poly(DBA-DTT)-BA (**7**) and (d) poly(DBC-DTT)-BA (**8**)

Table 1 Number-average molecular weight $\bar{M}_n$, intrinsic viscosity $[\eta]$ and solubility data for polymers **1–8**

Sample	$\bar{M}_n$[a]	$[\eta]$[b] ($dl\ g^{-1}$)	Solubility[c]
Poly(BBA-DTT) (**1**) (ref. 1)	12 600[d]	–[e]	(H–L)
Poly(BBC-DTT) (**2**) (ref. 1)	5900[f]	–[e]	(H–L)
Poly(DBA-DTT) (**3**) (ref. 1)	10 300	0.15	D–I, (L)
Poly(DBC-DTT) (**4**) (ref. 1)	7500	0.08	(B, C), D–I, (L)
Poly(BBA-DTT)-BA (**5**)	15 500	0.34	A(sw), F–I
Poly(BBC-DTT)-BA (**6**)	7100	0.15	(A), D–I
Poly(DBA-DTT)-BA (**7**)	10 400	0.15	A–L
Poly(DBC-DTT)-BA (**8**)	8700	0.11	A–L

[a] From osmometry, solvent $CHCl_3$

[b] In $CHCl_3$ as solvent at 30°C

[c] Solvents tested: A, acetone; B, benzene; C, toluene; D, tetrahydrofuran; E, dioxane; F, methylene dichloride; G, chloroform; H, dimethyl sulfoxide; I, *N,N*-dimethylformamide; L, benzyl alcohol; M, acetonitrile. Letters in parentheses indicate solubility at θ near the boiling point of the solvent; (sw): swells

[d] Calculated from the number-average degree of polymerization of the acetalized polymer **5**

[e] Insoluble in $CHCl_3$

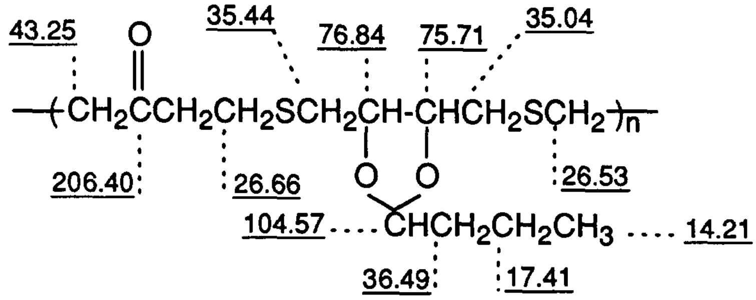
[f] Calculated from the number-average degree of polymerization of the acetalized polymer **6**

N.m.r. characterization

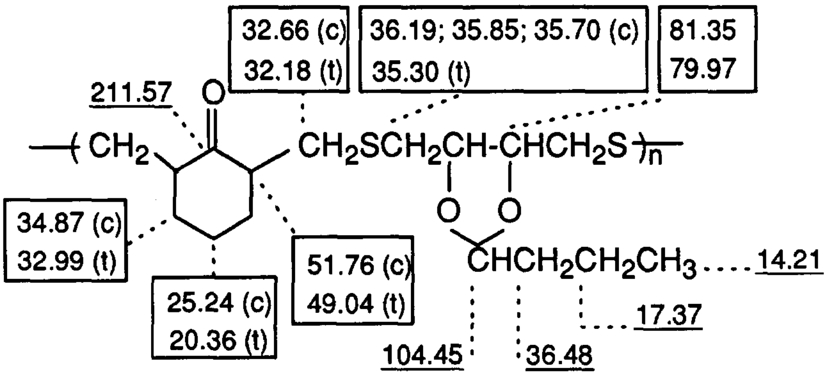
The formation of a 1,3-dioxolane ring along the backbone, due to the acetalization of hydroxyl groups of DTT moieties of polymers by butyraldehyde, gave rise to doubling of ^{13}C n.m.r. signals of the homochiral (*R,R*) carbon atoms of the main chain belonging to the newly formed ring. In fact, the above asymmetric centres become diastereotopic and hence magnetically unequivalent. Such an unequivalence, expressed in terms of relative difference of chemical shifts, is transmitted, with a decreasing effect on increasing the distance, also to the carbon atoms of the main chain bonded to positions 4 and 5 of the dioxolane ring[5]. Accordingly, poly(BBA-DTT)-BA (**5**) and its low-molecular-weight analogue (MVK-DTT)-BA (**9**) (*Table 2* and *Figure 2*), not containing any further asymmetric centre in addition to those of the DTT moieties, both exhibit doubling of the signals corresponding to the $-CH_2SCH_2CH-$ moiety.

Table 2 ^{13}C n.m.r. chemical shifts (ppm from tetramethylsilane) of poly(BBA-DTT)-BA (**5**), poly(BBC-DTT)-BA (**6**), poly(DBA-DTT)-BA (**7**) and poly(DBC-DTT)-BA (**8**) (c and t refer to peaks of *cis* and *trans* isomer, respectively)

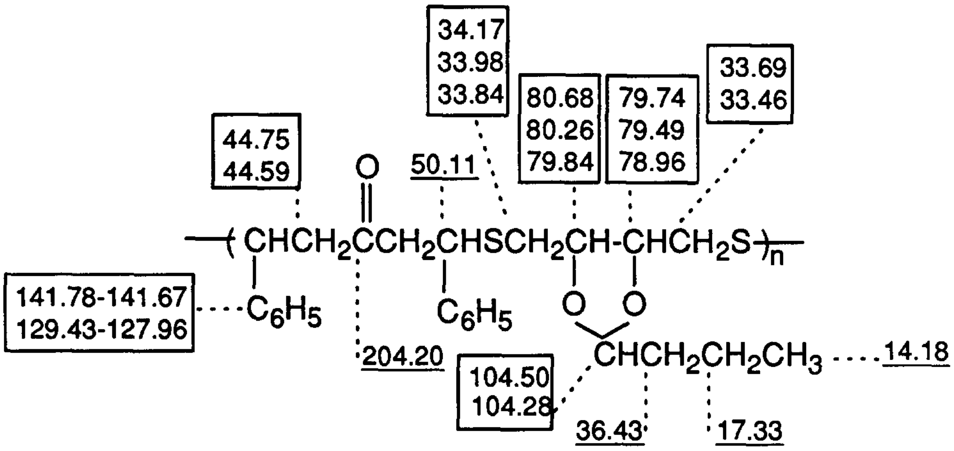
Poly(BBA-DTT)-BA (**5**):



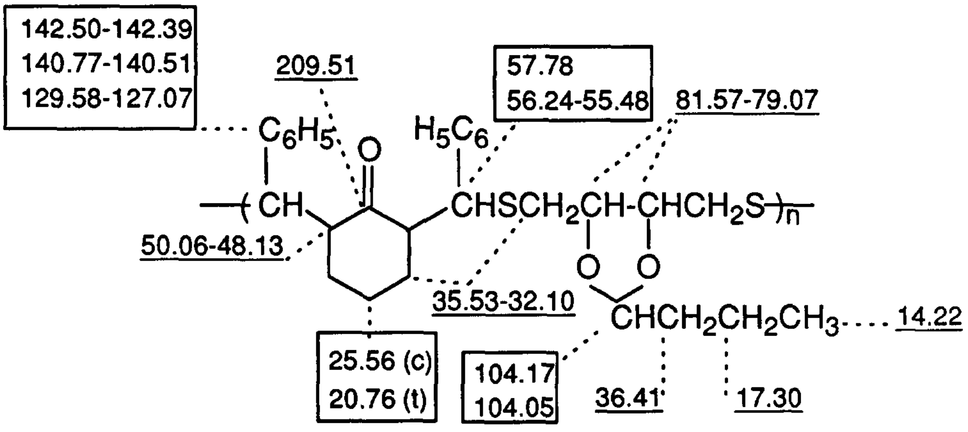
Poly(BBC-DTT)-BA (**6**):



Poly(DBA-DTT)-BA (**7**):



Poly(DBC-DTT)-BA (**8**):



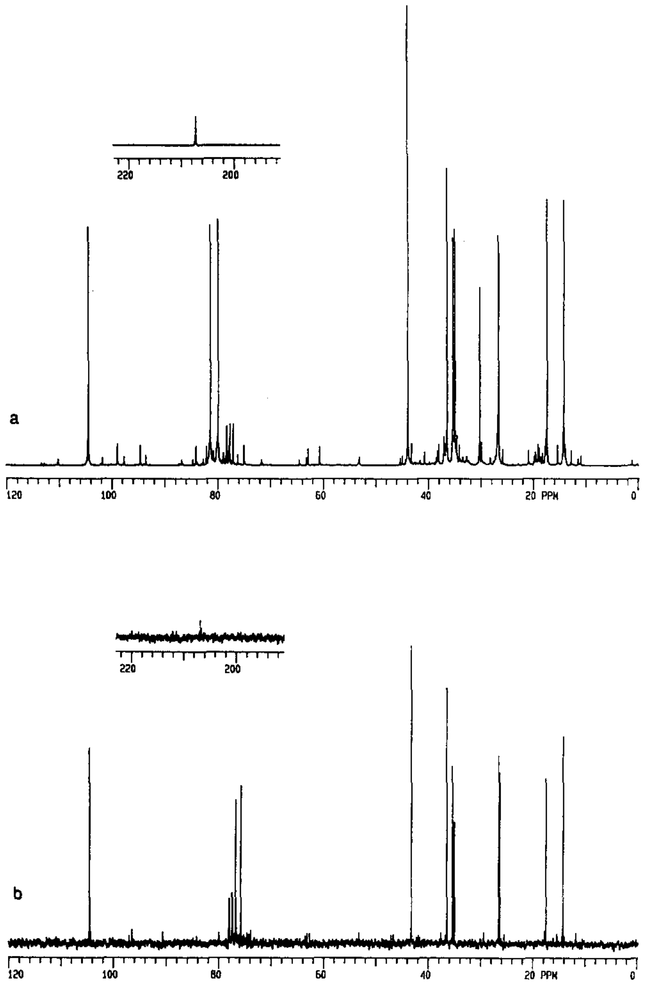


Figure 2 ^{13}C n.m.r. spectra of (a) (MVK-DTT)-BA (**9**) and (b) poly(BBA-DTT)-BA (**5**)

Thus, when new asymmetric centres giving rise to sequences of diastereomeric repeating units along the polymer chain are formed, the non-equivalence induced by the dioxolane ring combined with the spin multiplicity determined by the asymmetric centres of different configurations, generate even more complex spectra. Indeed, the ^{13}C n.m.r. spectrum of poly(DBA-DTT)-BA (**7**) (*Table 2* and *Figure 3*) shows for the ethereal –CH–O– carbon atoms both the splitting due to the presence of diastereomeric repeating units, with intensity ratios ca. 25/46/29 [practically the same as the above reported values for the precursor poly(DBA-DTT)[1]], and the doubling caused by the non-equivalence induced by the dioxolane ring. By contrast, the signal of the acetal O–CH–O, which is unaffected by the anisotropy induced by the dioxolane ring[5], shows two peaks (intensity ratio ca. 44/56) due to the diastereomeric repeating units having different chemical shifts disposed along the polymer chain. The same is found for the CH_2 bonded to the carbonyl group, exhibiting two peaks with intensity ratio ca. 46/54, as these methylene groups occur too far away from the dioxolane ring to be affected by its magnetic anisotropy.

Poly(BBC-DTT)-BA (**6**) and poly(DBC-DTT)-BA (**8**) (*Table 2*) gave very complicated ^{13}C n.m.r. spectra so that a complete assignment of all the signals was not possible. However, it was possible to measure the same ratios of diastereomeric repeating units having the *cis* or *trans* relative configuration of the cyclohexanone ring (ca. 88/12 and 75/25, respectively) as determined in the pristine poly(BBC-DTT) and poly(DBC-DTT)[1]. This result confirms that acetalization of the hydroxyl groups of polymers does not affect the relative amounts of diastereomeric repeating units. A further demonstration of this was offered by the acetalization of the low-molecular-weight analogue of poly(BBC-DTT), MMC-DTT (diastereomeric mixture), to give (MMC-DTT)-BA (**10**). The ^{1}H n.m.r. of this latter compound (see Experimental) showed in fact the same 50/50 ratio among diastereomers found in the starting material, and its ^{13}C n.m.r. spectrum (*Figure 4*) exhibited the expected additional splittings due to the magnetic anisotropy induced by the dioxolane ring.

Chiroptical properties

Compared with the corresponding hydroxy derivatives, which in $CHCl_3$ solution gave negative molar optical rotatory power values [Φ], increasing in absolute value on decreasing wavelength from 589 to 405 nm[1], acetalized polymers **5**–**8** showed an opposite behaviour, the optical rotatory power values appearing increasingly positive or decreasingly negative in the same wavelength region (*Table 3*). An analogous trend was observed in the low-molecular-weight acetalized derivatives, except for (MBC-DTT)-BA (**12**), which was the only compound exhibiting increasingly negative values of [Φ] on going towards shorter wavelengths (*Table 3*). Due to the large distance from the wavelengths where the absorption

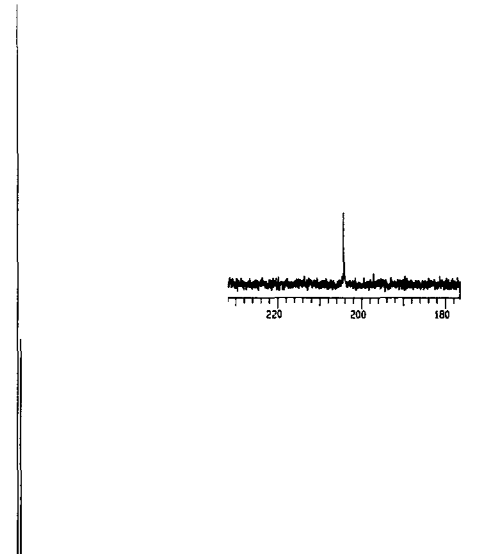


Figure 3 ^{13}C n.m.r. spectrum of poly(DBA-DTT)-BA (7). Asterisks refer to unsaturated end groups

maxima of the chromophores present in the repeating units are located, the optical rotatory dispersion curves appear plain, with no evidence of possible induced Cotton effects related to the existence of conformational homogeneity of the macromolecules in solution.

Indeed, the u.v. spectra in $CHCl_3$ of **5**–**8** (*Table 4* and *Figure 5a*) showed absorption maxima at 280–295 nm, related to the $n \rightarrow \pi^*$ electronic transition of the carbonyl chromophore[6], as well as at around 244 nm, due to the $n \rightarrow \sigma^*$ transition of the sulfide moiety[7,8]. When present (polymers **7** and **8**), the phenyl ring exhibited shoulders at 260–268 nm, connected with the lowest energy $\pi \rightarrow \pi^*$ electronic transition (^1L_b) of the aromatic chromophore[9].

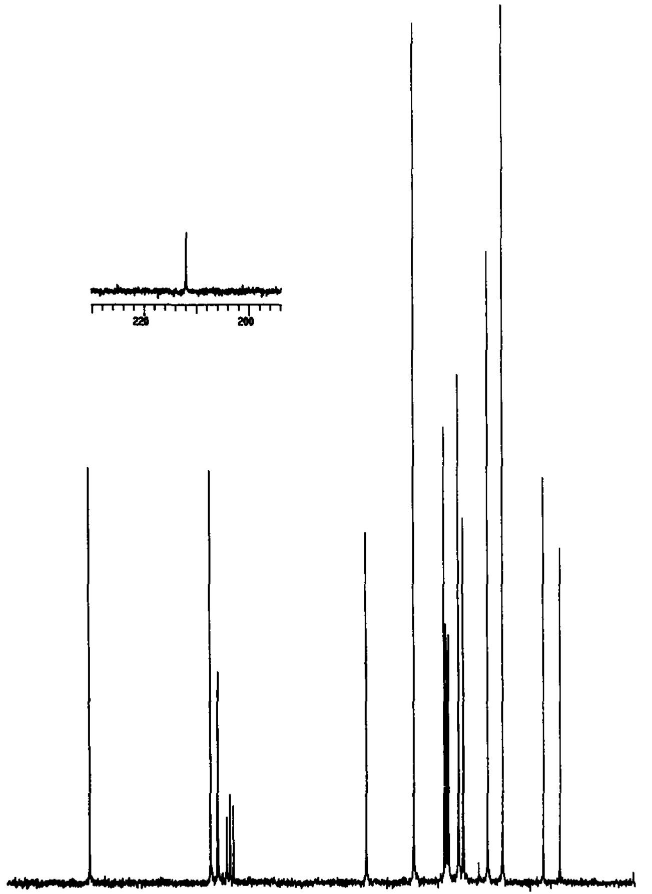
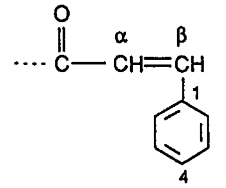
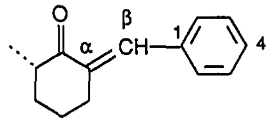


Figure 4 ^{13}C n.m.r. spectrum of (MMC-DTT)-BA (**10**)

As shown in *Table 4*, polymers **7** and **8** displayed in the $n \rightarrow \pi^*$ transition region ε values much higher than expected for saturated aliphatic ketones, similar to those observed for the previously measured hydroxy polymeric precursors **3** and **4**[1]. In that case the above findings were proved to be originated by the presence of α,β-unsaturated carbonyl end groups exhibiting a very high molar absorption coefficient due to conjugation with the phenyl ring (styryl ketone system), as depicted below. The same still holds for polymers **7** and **8**, as acetalization of the hydroxy groups of DTT moiety does not affect the other functionalities present in the macromolecules. Indeed, the ^{13}C n.m.r. spectrum of poly(DBA-DTT)-BA (**7**) (*Figure 3*) showed low-intensity peaks at ca. 144, 135, 131 and 126 ppm, attributable[1] to C_β, C-1, C-4 and C_α carbon atoms, in that order, of the styryl ketone system.





A similar pattern was also observed for poly(DBC-DTT)-BA (**8**), which showed the corresponding signals at 138–136 (three peaks) and 131 ppm. Assuming that the value of $\varepsilon = 23\,100\ l\ mol^{-1}\ cm^{-1}$ for the absorption band at 294 nm for the styryl ketone[1] system remains unchanged on passing from the low-molecular-weight models to the polymers, about two and one unsaturated end groups per macromolecule can be estimated for poly(DBA-DTT)-BA (**7**) and poly(DBC-DTT)-BA (**8**), respectively, on the basis of their $\bar{M}_n$ values (*Table 1*). The same result was previously obtained for the precursors poly(DBA-DTT) and poly(DBC-DTT).

C.d. spectra of polymers **5**–**8** (*Table 4*, *Figure 5b*) show dichroic bands strictly related to their u.v. absorption features, thus indicating that the chromophores of the repeating units are chirally perturbed. The Δε values, as far as the $n \rightarrow \pi^*$ electronic transition of the carbonyl chromophore is concerned, exhibit higher absolute values and a change of sign on passing from acetone to cyclohexanone derivatives (see **5** *versus* **6** and **7** *versus* **8**). Moreover, the presence of phenyl rings in the repeating units produces an increase of the absolute value of Δε (see **5** *versus* **7** and **6** *versus* **8**) referred to the band

Table 3 Molar optical rotatory power values $[\Phi]^{25}$ at various wavelengths for polymers **5**–**8** and low-molecular-weight compounds **9**–**12**

	$[\Phi]^{25}$ (deg dm^{-1} mol^{-1} cm^3)				
Sample	589 nm	578 nm	546 nm	435 nm	405 nm
Poly(BBA-DTT)-BA (**5**)	+29.0	+31.1	+36.9	+70.5	+85.2
Poly(BBC-DTT)-BA (**6**)	+32.0	+32.7	+40.3	+81.5	+95.1
Poly(DBA-DTT)-BA (**7**)	+5.5	+7.5	+8.4	+25.6	+30.4
Poly(DBC-DTT)-BA (**8**)	−13.5	−13.5	−14.5	−10.4	−5.0
(MVK-DTT)-BA (**9**)	+34.4	+37.0	+43.2	+81.1	+99.4
(MMC-DTT)-BA (**10**)	+39.3	+44.6	+50.6	+94.0	+114.9
(MBA-DTT)-BA (**11**)	−22.2	−21.1	−23.3	−23.4	−18.2
(MBC-DTT)-BA (**12**)	−92.6	−99.5	−111.4	−180.9	−228.6

Solvent $CHCl_3$ (concentration, $c = 1\ g\ dl^{-1}$), cell path length 1 dm. Values of polymers refer to one repeating unit

Table 4 Molar (decadic) absorption coefficients ε (wavelengths λ_{max} in parentheses) of u.v. absorption maxima and differential molar (decadic) absorption coefficient $\Delta\varepsilon$ (wavelengths λ in parentheses) of circular dichroism maxima of polymers **5**–**8** and of low-molecular-weight compounds **9**–**12** in $CHCl_3$ solution

	ε (l mol^{-1} cm^{-1}) and λ_{max} (nm)[a]			$10^2 \times \Delta\varepsilon$ (l mol^{-1} cm^{-1})[a]		
Polymer	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	$n \rightarrow \sigma^*$	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	$n \rightarrow \sigma^*$
Poly(BBA-DTT)-BA (**5**)	100 (280)	-	370 (243)	−1.4 (282)	-	−7.5 (237)
Poly(BBC-DTT)-BA (**6**)	145 (295)	-	487 (244)	+4.3 (294)	-	−6.8 (242)
Poly(DBA-DTT)-BA (**7**)	2150 (294)	1630 (sh, 268) 1650 (sh, 260)	2110 (244)	−5.4 (294)	−7.7 (272)	n.d. (+)[b]
Poly(DBC-DTT)-BA (**8**)	980 (295)	1150 (sh, 268) 1620 (sh, 262)	2490 (244)	+15.0 (300)	−7.5 (266)	n.d. (+)[b]
(MVK-DTT)-BA (**9**)	86 (285)	-	516 (240)	+0.2[c] (290)	-	−11.1 (242)
(MMC-DTT)-BA (**10**)	98 (285)	-	486 (242)	+0.6[c] (290)	-	n.d. (−)[b]
(MBA-DTT)-BA (**11**)	248 (sh, 285)	610 (sh, 268) 1050 (sh, 262)	2100 (245)	+12.8[c] (288)	−10.4 (sh, 260)	−81.0 (244)
(MBC-DTT)-BA (**12**)	290 (sh, 295)	745 (sh, 268) 1100 (sh, 262)	2260 (245)	+4.2[c] (290)	−2.8 (sh, 260)	n.d. (−)[b]

[a] sh: Shoulder

[b] n.d. (+), n.d. (−): Not detectable (positive or negative value of $\Delta\varepsilon$, respectively)

[c] $\Delta\varepsilon$ value related to one carbonyl chromophore per mole

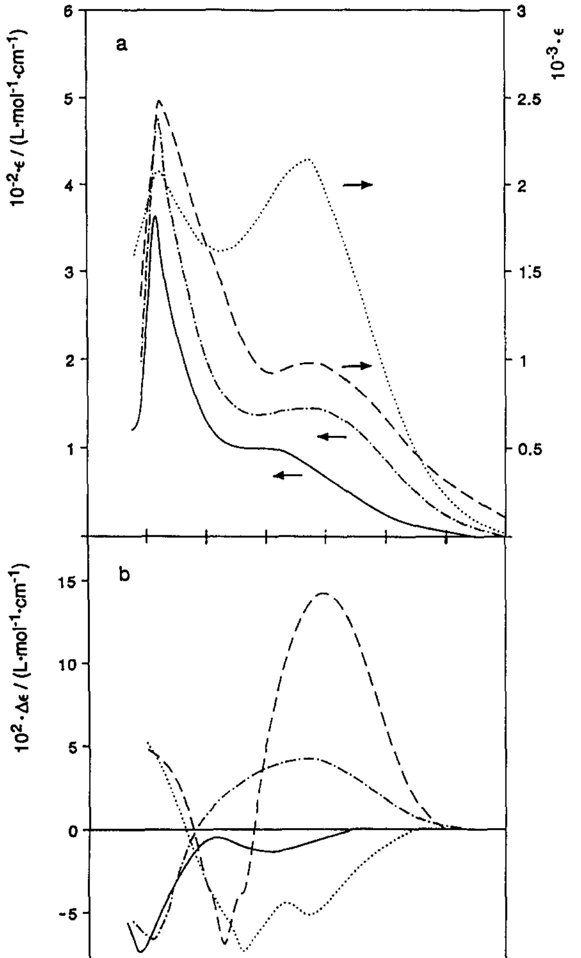


Figure 5 (a) U.v. and (b) c.d. spectra in $CHCl_3$ of poly(BBA-DTT)-BA (**5**) (——); poly(BBC-DTT)-BA (**6**) (–·–·); poly(DBA-DTT)-BA (**7**) (···); and poly(DBC-DTT)-BA (**8**) (– – –)

associated with the $n \rightarrow \pi^*$ electronic transition, the appearance of a negative structured band located at around 270 nm, connected with the ^1L_b electronic transition of the phenyl chromophore, and finally an inversion of sign in the band related to the $n \rightarrow \sigma^*$ electronic transition of the sulfide moiety near 240 nm. These phenomena appear to be due to a stiffening of the macromolecules arising from an enhancement of steric hindrance along the polymer backbone as a consequence of the introduction of the phenyl ring. However, comparison of $10^2 \times \Delta\varepsilon$ values at 294 nm of polymers **7** and **8** with the corresponding values previously[1] obtained from the precursors poly(DBA-DTT) and poly(DBC-DTT) (+8.8 and +29.8 l mol^{-1} cm^{-1}, respectively) shows a lowering of $\Delta\varepsilon$ on acetalization of the hydroxy groups of DTT moieties. This occurrence could be ascribed to a higher conformational rigidity of the polymeric precursors with respect to the functionalized derivatives containing the dioxolane rings, probably due to the presence of intramolecular hydrogen bonding by the hydroxy groups located along the main chain. In fact, the diastereomeric content of the repeating units cannot affect the ellipticity of the bands, as the configurational situation along the macromolecules remains unchanged on acetalization, as proved by the n.m.r. results. The unavailability of c.d. data for poly(BBA-DTT) and poly(BBC-DTT), due to their insolubility[1], unfortunately prevents an analogous comparison with $\Delta\varepsilon$ values of the corresponding acetalized polymers **5** and **6**. In the low-molecular-weight analogues, also, a decrement of $\Delta\varepsilon$ related to the $n \rightarrow \pi^*$ transition is observed on passing from MBA-DTT and MBC-DTT[1] to (MBA-DTT)-BA and (MBC-DTT)-BA (*Figure 6*) and an analogous occurrence, although less evident, is found when MVK-DTT and MMC-DTT[1] are compared with (MVK-DTT)-BA and (MMC-DTT)-BA (*Figure 7*). On the basis of c.d. measurements, therefore, the acetalization of polymers **1**–**4** appears to produce only local conformational modifications rather than the stabilization by cooperative effects of a single conformation having a prevailing

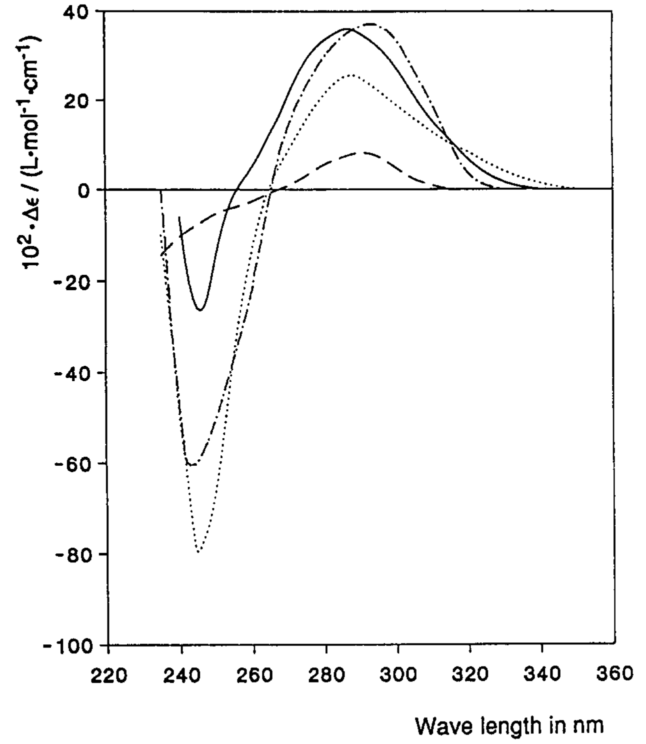


Figure 6 C.d. spectra in $CHCl_3$ of MBA-DTT (——), MBC-DTT (-·-·), (MBA-DTT)-BA (**11**) (···) and (MBC-DTT)-BA (**12**) (---)

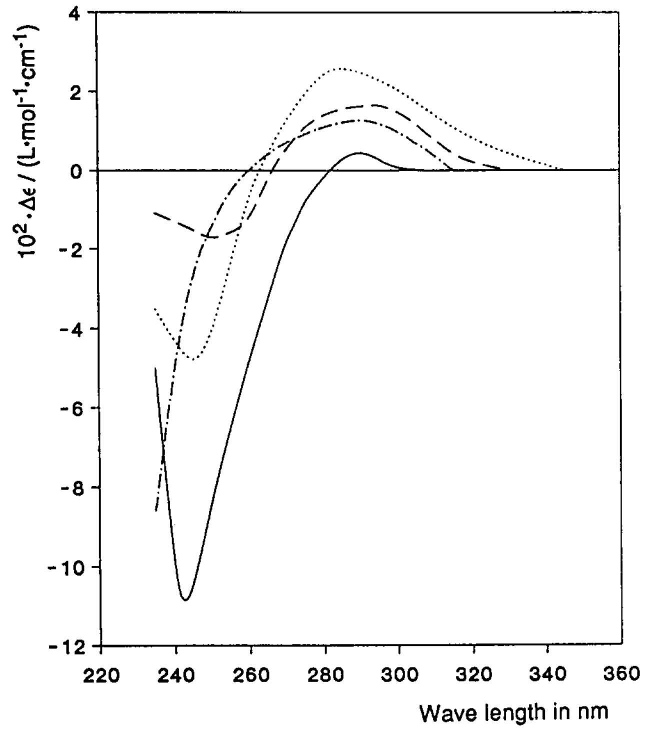


Figure 7 C.d. spectra in $CHCl_3$ of MVK-DTT (···), MMC-DTT (---), (MVK-DTT)-BA (**9**) (——) and (MMC-DTT)-BA (**10**) (-·-·)

chirality extended to the whole macromolecule. In fact, no remarkable chiroptical effects, such as, for example, exciton splittings, induced in the c.d. spectral region associated with the $n \rightarrow \pi^*$ electronic transition of ketone chromophore, are observed. In particular, the lack of a couplet around 280 nm in poly(BBA-DTT)-BA, which contains only asymmetric centres having the same absolute configuration (originated by the L-dithiothreitol moiety), suggests a low conformational rigidity, thus preventing the formation of an ordered dissymmetric secondary structure.

CONCLUSIONS

The acetalization by butyraldehyde of optically active poly(γ-ketosulfide)s containing the L-dithiothreitol moiety, proceeds under mild conditions with good yields. As the functionalized polymers are soluble in the most common organic solvents, spectroscopic structural characterizations as well as viscosity and molecular weight determinations have been readily performed.

The n.m.r. measurements on poly(BBC-DTT)-BA, poly(DBA-DTT)-BA and poly(DBC-DTT)-BA confirm that the reaction with butyraldehyde does not affect the diastereomeric distribution of the repeating units along the polymer chains, which was substantially random in the polymeric precursors. As a consequence, the c.d. spectra are the result of the superimposition of different chiral contributions by the various diastereomeric repeating units in the macromolecules, in the absence of a large conformational dissymmetry, as revealed by the lack of exciton splittings. Even poly(BBA-DTT)-BA, constituted of sequences all having the same configuration, does not show any c.d. couplet, in accordance with a rather large conformational mobility preventing the stabilization of an ordered secondary structure with one single chirality.

ACKNOWLEDGEMENTS

Financial support by MURST (Fondi 60%) is gratefully acknowledged.

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