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Functional polythiiranes 4

Preparation and polymerization of poly(ethylene oxide) macromonomers

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Summary

New polymers with polythiiranes main chains and PEO side chains have been prepared by ring opening polymerization of the corresponding thiirane monomers. These polymers were characterized by ^1H and ^{13} C NMR and their average molecular weight were studied by SEC. For side chains containing three or more EO units, the polymers were soluble both in water and in organic solvents.

Introduction

The multiple properties of poly(ethylene oxide) PEO are customarily used for various practical applications in the scope of biotechnologies, ionic conductivity, cation-binding (1,2,3). Comb-like structures of PEO bonded to a polymer backbone have been obtained by various ways including grafting (4), macromonomers synthesis (5,6) or copolymerization (7) and have led to amphiphilic copolymers. Several types of main chain units have been associated with PEO side chains, mostly vinylic and acrylic, but sulfur containing backbones have not been used till now. In previous papers (8,9,10) we have described the synthesis of polythiiranes bearing as side chain different substituents with various properties. For some potential applications, we are looking for water soluble polythiiranes. Thus we have attempted to prepare polythiiranes with PEO side chains from thiirane macromonomers.

This paper reports the synthesis of such PEO macromonomers (**1-9**). Bis-macromonomers **10** and **11** have been also prepared for further hydrogels studies.

Both ester and ether groups have been considered as link between the polymerizable thiirane group and the side chain; the ester macromonomers were in fact easier to prepare but will be more sensitive to hydrolysis reactions in further applications. Results dealing with homopolymerizations of these macromonomers with tetramethyl ammonium dithiobenzoate as an initiator are also reported in this paper.

Experimental section

^1H and ^{13}C NMR spectra were recorded on a Brucker AC 400 spectrometer in $CDCl_3$ as solvent and TMS as reference. FT-IR spectra were obtained on a Fourier transform Perkin Elmer 1750 infrared spectrometer. SEC measurements were performed on Styragel columns (Waters) in THF as eluent; molecular weights were reported as the molecular weights of equivalent elution volume of polystyrene samples. Light-scattering measurements have been carried out on a Malvern 4700 apparatus.

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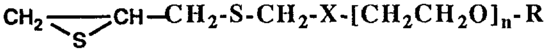
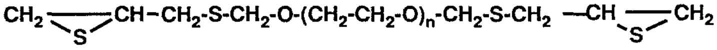


1: X = COO n =1 R = CH_3
2: X = COO n =1 R = C_2H_5
3: X = COO n =2 R = CH_3
4: X = COO n =3 R = CH_3
5: X = COO n =4 R = CH_3
6: X = COO n =7 R = CH_3
7: X = O n = 1 R = CH_3
8: X = O n = 3 R = CH_3
9: X = O n = 4 R = CH_3



10 : n = 3
11 : n = 4

Bromoacetates . Monomethyl ether of the glycol (0.1mol) and dry pyridine were dissolved in dry diethylether (150 mL) and the solution cooled in an ice bath. Bromoacetylbromide (0.1 mol) was slowly added to the mixture; at the end of the addition the reaction mixture was left overnight at room temperature; the precipited pyridinium salt was filtered off and the organic phase was worked up as customarily (Yields : 70-80%). The products, colorless oils, were purified by distillation: n=1, R=CH_3: E(30mm)= 100°C; n=2, R=C_2H_5: E(20mm) = 110°C; n=2, R=CH_3: E(30mm)= 156°C; n=3, R=CH_3: E(1mm)= 143°C; n=4, R=CH_3: E(0.01mm)= 150°C, except the bromoacetate with n≈7 which was chromatographied on silica gel in cyclohexane/ether mixtures. ^1H NMR spectra were nearly identical with those of the methylether of the glycol with the addition of signals at 3.89 ppm corresponding to the Br CH_2CO protons and 4.30 ppm for $COOCH_2$ protons.

IR (film) : ν (cm^{-1}) = 1735: (C=O, str), 1285: (C(O)-O, str); 1110-1120 :(-O-CH_2CH_2, str)

Chloromethylethers . 2-methoxyethoxymethyl chloride was commercially available from Janssen. Other chloromethyl ethers and bis-chloromethyl ethers were prepared according to (11) by chloromethylation of the corresponding glycol monomethylether using paraformaldehyde and gaseous hydrochloric acid ; they were immediatly purified by distillation: n=3, R=CH_3: E (1mm)= 115°C; n=4, R=CH_3: E (0.01mm)= 160°C; bis, n=3: E (1mm)= 120°C; bis, n=4: E (0.01mm)= 158°C and stored at -20°C (Yields:30-50%). Their NMR spectra were also nearly identical with those of the corresponding glycol monomethylether except the addition of a signal at 5.58 ppm corresponding to the $ClCH_2$ protons.

Macromonomers . Mercaptomethyl thiirane (MMT) was prepared according to (12). Bromoesters and chloromethylethers were reacted with MMT in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) under the experimental conditions previously reported (9); high yields of crude products were observed (> 80%). The oily macromonomers were purified by silica gel chromatographies with cyclohexane/ether mixtures as eluant. The molecular weight of some macromonomers were measured by SEC: **5**: M_n= 310, M_w = 335, (calculated M = 354); **6**: M_n= 464, M_w= 512, (calculated M_n from ^1H NMR= 464); **8**: M_n = 210, M_w = 225, (calculated M = 282)

The chemical shifts of the carbon and hydrogen atoms in the macromonomers for ^{13}C and ^1H NMR of were found characteristic of their structures; the chemical shifts for the atoms in the side-chains are identical to those described in table 2; furthermore, slight differences have appeared between ester and ether macromonomers. The protons of the 2,3-epithiopropyl group give rise to the usual pattern in ^1H NMR which was confirmed by a 2D correlation; δ(ppm): for ester macromonomers: 2.28 (d, 1H : methylene of thiirane), 2.58 (d, 1H : methylene of thiirane, 2.65-2.75 (m, 1H : methylene of the chain), 3.05-3.15 (m, 2H : methine of the thiirane and methylene of the chain); for ether macromonomers: 2.30 (d, 1H : methylene of thiirane), 2.55-2.65 (m, 2H : methylene of thiirane and methylene of the chain), 3.08-3.20 (m, 2H: methylene of the chain and methine of the thiirane). The carbon atoms of the 2,3-epithiopropyl group gave rise to the following signals: δ(ppm) 25.80, 33.34, 38.50 for ester macromonomers and 26.30, 34.20, 37.2 for ether macromonomers corresponding respectively to methylene of thiirane, methine of thiirane and methylene of the chain.

Homopolymerizations . Macromonomers were polymerized with different amounts of tetramethylammonium dithiobenzoate (table 1) in DMF as previously described (9); the polymers were precipitated in diethylether, dissolved in THF and reprecipitated in diethylether and dried.

Results and discussion

Macromonomers synthesis. The synthesis of the ester macromonomers were run according to the previously described method (9) from mercaptomethylthiirane (MMT) and the bromoacetic esters of the monomethylether of ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, and PEO (M_n =350). Bromoacetate of PEO 350 have led in some cases to macromonomer **6** of lower purity than the other macromonomers: the stoechiometry of the reaction is harder to control than in the case of glycols of well-defined molecular weight. The bromoacetates were prepared from bromoacetyl bromide and the corresponding monomethoxylated glycols and are described in the experimental part. The synthesis of the ethers was run in the same way but with chloromethyl ethers in place of bromoacetates. The chloromethyl ethers were prepared from monomethyl ether of the glycol and formaldehyde in the presence of hydrochloric acid (11) as described in the experimental part. Both types of macromonomers were obtained with high yields (>80%). Their ^{13}C and ^1H NMR spectra described in the experimental section have confirmed the expected structures.

Homopolymerizations. These macromonomers were polymerized with tetramethylammonium dithiobenzoate as an initiator and with DMF as a solvent (9). The results of these polymerizations are collected in table 1. The polymers were produced in very high yields in all cases. Monomers **1**, **2**, **7** with n =1 were studied as models for spectral data and behave very similarly to methyl(2,3-epithiopropyl) thioethanoate whose polymerization was previously studied (9).

The average molecular weights were obtained by SEC using a polystyrene calibration curve. For high $[M_0]/[I_0]$ ratios the DP_n measured by SEC are nearly in accordance with those calculated for a living polymerization; but, as previously described (13), for lower ratios the DP_n measured by SEC are higher than those calculated. The chromatograms of polymers obtained from **3**, **4**, **5**, **6**, **8**, **9** were dissymetrical with a short front and a large tail that suggest reversible adsorption superimposed to size exclusion; DP_n are low and appear to be independant of the $[M_0]/[I_0]$ ratios ; the longer the PEO chain the lower is the DP_n observed. It is well known (4, 5, 14) that comb polymers present a decrease of their hydrodynamic volume; thus the molecular weights must have been severely underestimated by SEC.

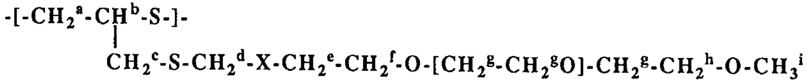
Methoxypoly(ethylene oxide) acrylate and methacrylate have led by free radical polymerization to "self-gelling" polymers (6,15). In our experiments, an irreversible gel was obtained in only one case with an highly concentrated solution of monomer **6**. The formation of a gel in these conditions might be related with the presence of slight traces of bifunctional monomer: commercial methoxylated glycols may contain some amounts of non-reacted glycol which are hard to eliminate. The high polydispersity indexes exhibited for polymers of products **5** and **9** may be related to the same reason. On the other hand, the copolymerization of monomer **8** with 4 to 6 % mole of the bifunctional monomers **10** and **11** have afforded the expected gels.

Table 1: Polymerizations results : M_0 : monomer concentration, I_0 : initiator concentration, $[M_0/I_0] = 0.5$ mole l^{-1}, DP_n: number average degree of polymerization, M_n: number average molecular weight, I : polydispersity index , DMF, t = 20°C

Monomer	$[M_0/I_0]$	Yield %	DP_n by SEC	Mn 10^{-3} by SEC	I
1	200	95	165	36.6	1.8
n = 1	100	90	129	28.5	1.6
	50	96	101	22.4	1.7
	33	94	83	18.5	2.0
2	500	90	324	76.6	1.9
n = 1	400	95	321	75.6	1.9
	208	98	240	56.6	2.0
	102	95	168	39.8	1.8
	51	95	113	26.7	2.1
3	200	76	77	20.6	1.4
n = 2	100	80	68	18.0	1.6
	49	78	52	13.9	1.8
	33	75	45	13.1	2.2
4	400	97	66	20.4	2.1
n = 3	200	98	64	17.7	2.0
	133	97	78	24.0	2.6
	66	96	65	20.0	2.4
5	400	91	56	20.0	3.7
n = 4	200	88	60	21.3	3.5
	100	84	44	15.5	2.1
	50	85	31	11.0	4.2
6	204	70	16	8.2	1.6
n ≈ 7	102	70	17	8.4	1.5
	50	72	18	9.0	1.4
	33	76	18	9.0	1.4
7	401	96	391	75.9	1.9
n = 1	200	98	251	56.5	2.1
	102	98	182	42.9	2.0
8	400	90	101	28.4	1.4
n = 3	200	95	42	28.0	1.5
	100	92	88	24.9	1.5
	50	90	80	22.6	1.5
9	200	86	81	26.6	3.7
n = 4	100	83	61	20.0	3.5
	66	78	74	24.4	2.5

Table 2 : 1H NMR data of polymers in CDCl3

Type of protons	a	b	c	d	e	f	g	h	i
Polymers 1 ; n=1	2.95-3.02 m, 2H	3.10-3.20 m, 1H	3.03-3.10 m, 2H	3.36 s, 2H	4.30 t, 2H	3.63 t, 2H			3.38 s, 3H
3 ; n=2	2.95-3.03 m, 2H	3.10-3.20 m, 1H	3.03-3.10 m, 2H	3.36 s, 2H	4.30 t, 2H	3.72 t, 2H	3.66 t, 2H	3.57 t, 2H	3.38 s, 3H
4 ; n=3	2.95-3.03 m, 2H	3.10-3.20 m, 1H	3.03-3.10 m, 2H	3.36 s, 2H	4.30 t, 2H	3.72 t, 2H	3.60-3.70 m, 6H	3.55 t, 2H	3.38 s, 3H
5 ; n=4	2.95-3.03 m, 2H	3.10-3.20 m, 1H	3.03-3.10 m, 2H	3.35 s, 2H	4.31 t, 2H	3.72 t, 2H	3.60-3.70 m, 10H	3.55 t, 2H	3.38 s, 3H
6 ; n= 7	2.95-3.03 m, 2H	3.10-3.20 m, 1H	3.03-3.10 m, 2H	3.34 s, 2H	4.31 t, 2H	3.72 t, 2H	3.60-3.70 m	3.55 t, 2H	3.38 s, 3H
7 ; n=1	2.93-3.03 m, 2H	3.08-3.18 m, 1H	2.93-3.08 m, 2H	4.76 s, 2H	3.65-3.75 m, 2H	3.55 t,2H			3.38 s, 3H
8 ; n=3	2.90-3.05 m, 2H	3.05-3.15 m, 1H	2.90-3.05 m, 2H	4.76 s, 2H	3.70-3.80 m, 2H	3.60- m,	3.70 8H	3.55 t, 2H	3.38 s, 3H
9 ; n=4	2.90-3.05 m, 2H	3.05-3.15 m, 1H	2.90-3.05 m, 2H	4.76 s, 2H	3.70-3.80 m, 2H	3.60- m,	3.70 12H	3.55 t, 2H	3.38 s, 3H

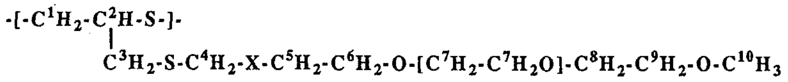


$$\text{-[-CH}_2{}^{a}\text{-CH}^{b}\text{-S-]-} \quad \text{(CH}^{b}\text{: } \text{CH}_2{}^{c}\text{-S-CH}_2{}^{d}\text{-X-CH}_2{}^{e}\text{-CH}_2{}^{f}\text{-O-[CH}_2{}^{g}\text{-CH}_2{}^{g}\text{O]-CH}_2{}^{g}\text{-CH}_2{}^{h}\text{-O-CH}_3{}^{i}\text{)}$$

X = COO :1,3,4,5,6 ; X = O : 7,8,9

Table 3: 13 C NMR data of polymers in CDCl3

Type of carbon	C1	C2	C3	C4	CO-O	C5	C6	C7	C8	C9	C10
Polymers 1 ; n=1	35.77	46.61-46.88	37.09	34.20	170.23	64.37	70.24				58.94
3 ; n=2	35.85	46.66	37.11	34.25	170.24	64.62	69.01		70.51	71.90	50.05
4 ; n=3	35.71	46.42-46.51 46.69-46.84	36.97	34.16	170.23	64.53	68.94	70.59	70.59	71.92	59.04
5 ; n=4	35.72	46.36-46.49 46.69-46.86	36.96	34.15	170.22	64.52	68.94	70.58	70.58	71.91	59.02
6 ; n=7	35.69	46.30-46.42 46.59-46.76	36.94	34.14	170.21	64.51	68.94	70.56	70.56	71.92	59.03
7 ; n=1	35.84	47.08-47.16 47.33-47.46	35.54	74.94		67.08	71.55				59.04
8 ; n=3	35.81	46.93-47.19 47.36-47.50	35.43	74.86		67.30	70.30	70.60	70.55	71.93	59.05
9 ; n=4	35.78	47.45-47.30	35.37	74.83		67.26	70.26	70.54	70.47	71.89	59.03



$$\text{-[-}C^1H_2\text{-}C^2H\text{-S-]-} \quad | \quad C^3H_2\text{-S-}C^4H_2\text{-X-}C^5H_2\text{-}C^6H_2\text{-O-[}C^7H_2\text{-}C^7H_2O\text{]-}C^8H_2\text{-}C^9H_2\text{-O-}C^{10}H_3$$

X = COO 1,3,4,5,6 ; X = O 7,8,9

The ^{13}C and ^{1}H NMR data of the polymers obtained from macromonomers **1**, **3**, **4**, **5**, **6**, **7**, **8**, **9** are reported in table 2 and are in accordance with their structure. The backbone structure has no effect on the chemical shifts of the side chains; the methine carbon C_2 presents, as customarily in these compounds, a triad effect: expanded spectra exhibit four signals apparently in the same ratios which involves a Bernouillan process for the polymerization. This result is somewhat different from previous observations on poly(methylthiirane) which has shown a different distribution of the four signals under identical experimental conditions of polymerization (16).

The hydrosolubility of the polymers is achieved for n=3 in both series but is higher for the ethers. These polymers are also soluble in various organic solvents and are thus amphiphiles.

The studies of the physical properties of the new macromolecules and of some applications are in progress.

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