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Polymer 42 (2001) 5973–5978

polymer

www.elsevier.nl/locate/polymer

A new route to carboxylated poly(ether sulfone)s: synthesis and characterization

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Received 22 November 2000; received in revised form 5 January 2001; accepted 10 January 2001

Abstract

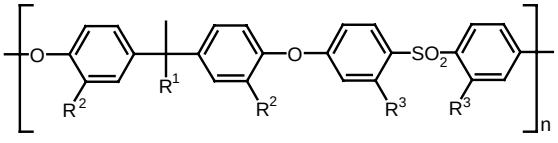
The copolymerization of 5-[(4-fluorophenyl)sulfonyl]-2-fluorobenzoic acid with bis(4-hydroxyphenyl)sulfone in 1,1-dioxothiolane with sodium carbonate as a base results in carboxylated poly(ether sulfone)s. The polycondensation polymerization, however, is associated with partial decarboxylation. Conversely, the copolymerization of 2,5-dihydroxybenzoic acid (hydroquinone carboxylic acid) with bis(4-fluorophenyl)sulfone under identical conditions results in a poly(ether ether sulfone) with quantitative decarboxylation.

Keywords: 5-[(4-fluorophenyl)sulfonyl]-2-fluorobenzoic acid; bis(4-hydroxyphenyl)sulfone; Carboxylated poly(ether sulfone)s

1. Introduction

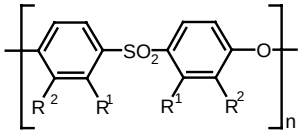
Aromatic poly(arylene ether sulfone)s are high performance thermoplastic materials which are extensively employed for the preparation of semi-permeable membranes [1–7]. While these materials have excellent overall properties, e.g. high thermal stability, good mechanical strength and chemical inertness (chemical resistance) under various conditions, gel formation on the membrane surface and in its pores often causes the fouling of ultrafiltration membranes. This phenomenon is especially prominent with hydrophobic polysulfone membranes. Hydrophilic membranes such as cellulose acetate, poly(vinyl alcohol) and polyacrylonitrile membranes have superior characteristics of less absorption of solutes and lower molecular weight cut-off compared to hydrophobic membranes. It is highly desirable to combine the advantages of the hydrophobic poly(arylene ether sulfone) membranes with the advantages of hydrophilic membranes.

Two of the most important technical poly(arylene ether sulfone)s are based on the repeating units **I** [Udel® (Amoco), Ultrason S® (BASF)] and **V** [Victrex® (ICI) and Ultrason E® (BASF)]. There are many routes for chemical modification of these membranes in order to make them more hydrophilic and sulfonation is one of the most often applied modifications. Recently for both polymer types **I** and **V** the carboxylated analogous **II**, **III**, **IV**, and **VI** with various degrees of substitution were reported in the literature.



I : $R^1 = CH_3$; $R^2 = R^3 = H$; **II:** $R^1 = CH_2CH_2COOH$; $R^2 = H$; $R^3 = H$;

III: $R^1 = CH_3$; $R^2 = COOH$; $R^3 = H$; **IV:** $R^1 = CH_3$; $R^2 = H$; $R^3 = COOH$;



V: $R^1 = R^2 = H$; **VI:** $R^1 = H$; $R^2 = COOH$; **VII:** $R^1 = COOH$; $R^2 = H$;

The introduction of pendent carboxylic acid groups into Udel® was realized by copolymerization of bis(4-chlorophenyl)sulfone or bis(4-fluorophenyl)sulfone with various amounts of bis(4-hydroxyphenyl)sulfone and the diphenolic acid 4,4-bis(4-hydroxyphenyl)valeric acid in *N*-methyl-2-pyrrolidone, using potassium carbonate as a base [8].

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Thus modified Udel® **II** with various amounts of pendent carboxylate groups became accessible.

Carboxylated Udel® **III** was prepared in a sequence of three polymer analogous reactions [9]: (i) Bromination of Udel® in chloroform at rt occurs in the bisphenol A moiety in the *ortho*-ether position. (ii) For the metallation of the dibromo-Udel® both the bromine and the *ortho*-sulphone position are potentially reactive, the first by metal–halogen exchange and the second by heteroatom directed lithiation. Both reactions occur, the metal–halogen exchange, however, being prevalent. (iii) Carboxylation of the lithiated Udel® finally results in the carboxylated polymer **III** with carboxylic acid groups in the bisphenol A moiety in *ortho* position to the sulfone in a ratio of 8:1.

Carboxy Udel® **IV** was obtained by a sequence of two polymer analogous reactions [10,11]. First, treatment of Udel® **I** with butyllithium in THF solution at temperatures < -10°C results in the lithiation of the *ortho*-sulfonyl site of Udel®. In the second step treatment with carbon dioxide results in the Li-carboxylated Udel® **IV**.

Preparation of carboxylated Victrex® **VI** is more difficult because of two reasons: direct lithiation and bromination were unsuccessful according to Guiver et al. [11]. Victrex® is soluble only in polar solvents, e.g. DMF, NMP, DMSO and TCE (1,1,2,2-tetrachloroethane) which are incompatible with lithiation agents; for electrophilic bromination in solution the aromatic system is not electron rich enough. In conformity with this observation, Guiver et al. found that bromination of Udel® occurs only in the *ortho*-ether position of the bisphenol A moiety and not in the *ortho*-ether position of the phenylsulfone moiety. In addition, they found that Victrex® does not react with bromine in solution under the conditions employed. However, Máthé et al. [12]found that direct bromination of Victrex® in the melt at elevated temperatures results in a brominated polyethersulfone with 0.3–2.3 bromine atoms per repeating unit in the *ortho*-ether position. The authors further claim that brominated Victrex® undergoes metal–halogen exchange with butyllithium in THF solution (brominated Victrex® is soluble in THF) and the reactive lithiated intermediates were quenched with carbon dioxide to result in carboxylated Victrex® **VI**. At this point it should be noted that in our laboratory Gehlen [13] found that upon treatment of brominated Victrex® with butyllithium a cross-linked polymer was obtained.

Carboxylated Victrex® **VII** was not mentioned in the literature to the best of our knowledge. In the present communication, we present results with respect to the preparation of carboxylated Victrex® **VI** with a degree of substitution (DS) <0.5 by a polycondensation route starting from 5-[(4-fluorophenyl)sulfonyl]-2-fluorobenzoic acid and bis(4-hydroxyphenyl)sulfone.

2. Experimental part

2.1. Materials

Starting materials and reagents used for the monomer synthesis and for polycondensation were of high purity. Bis(4-fluorophenyl)sulfon (Aldrich), bis(4-hydroxyphenyl)-sulfon (Merck), and 2,5-dihydroxybenzoic acid were used without further purification. All solvents were freshly distilled before use.

The monomer syntheses and polycondensations were carried out under nitrogen. Nitrogen was passed over molecular sieves and finely distributed potassium on aluminium oxide for purification.

2.2. Measurements

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 NMR spectrometer at 300 and 75 MHz, respectively. Deuterated dimethylsulfoxide (DMSO-d_6) was used as solvent and tetramethylsilane (TMS) served as internal standard.

Gel permeation chromatography (GPC) analyses were carried out using a high pressure liquid chromatography pump, a refractive index detector and an ultraviolet detector. The eluting solvent was *N*,*N*-dimethylacetamide (DMAc) with 1.220 g/l LiCl and a flow rate of 0.5 ml/min. Four columns with PL-gel from Polymer Laboratories were applied: length of the column: 300 mm, diameter 7.5 mm, diameter of gel particles 5 μm, nominal pore widths 100, 500, 10^3, and 10^4 Å. Calibration was achieved with polystyrene standards.

Cuprophan dialysing tubes (from Akzo-Nobel) type 20 145, code 86274-200001 with a size exclusion limit of 1000 Da for proteins in aqueous solutions were used.

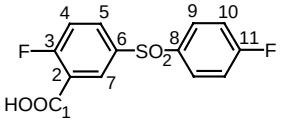
2.3. Monomer synthesis

2.3.1. 5-[(4-Fluorophenyl)sulfonyl]-2-fluorobenzoic acid **3**

A solution of bis(4-fluorophenyl)sulfone **1** (50.85 g, 0.2 mol) in dry THF was treated at −78°C with a solution of BuLi (2.5 M) in hexane (20 ml, 0.05 mol). The red solution of the lithiated bis(4-fluorophenyl)sulfone **2** was stirred for 30 min at −78°C and then allowed to warm up to −20°C within 1 h. The resulting brown suspension was cooled again to −78°C and treated with CO_2 (g) for 2 h. During this time the solution was allowed to warm up to 0°C and added to 200 ml water. THF was removed i.vac.; excess bis(4-fluorophenyl)sulfone crystallized and was separated by filtration. The solution of lithium 5-[(4-fluorophenyl)sulfonyl]-2-fluorobenzoate was acidified with dil. hydrochloric acid and cooled to 0°C. Crystals of 5-[4-fluorophenylsulfonyl]-2-fluorobenzoic acid were isolated by filtration and dried under reduced pressure. Yield 8.59 g (58%). Mp 186–188°C.

^{1}H NMR (DMSO-d_6): $\delta = 13.90$ (br. signal, 1H, COOH); 8.45 (dd, $J = 2.6$, 6.4 Hz, 1H, CH-7), 8.30 (ddd, $J = 2.6$, 4.5, 9.1 Hz, 1H, CH-5), 8.15 (AA′BB′X, $J = 5.3$, 8.7 Hz, 2H, CH-9), 7.64 (dd, $J = 10.6$, 9.1 Hz, 1H, CH-4), 7.52 (AA′BB′X, $J = 8.7$, 8.7 Hz, 2H, CH-10) ppm.

^{13}C NMR (DMSO-d_6): $\delta = 165.98$ (d, $J = 246.9$ Hz, C-3), 164.58 (d, $J = 264.8$ Hz, C-11), 164.29 (d, $J = 3.2$ Hz, C-1), 138.07 (d, $J = 3.2$ Hz, C-8), 137.62 (d, $J = 3.2$ Hz, C-6), 134.79 (d, $J = 11.6$ Hz, C-5), 132.33 (d, $J = 2.9$ Hz, C-7), 131.71 (d, $J = 9.5$ Hz, C-9), 121.62 (d, $J = 12.7$ Hz, C-2), 120.11 (d, $J = 24.3$ Hz, C-4), 118.00 (d, $J = 23.2$ Hz, C-10) ppm.



2.4. Polycondensation

2.4.1. Carboxylated poly(ether sulfone) 5

To a solution of bis(4-hydroxyphenyl)sulfone **4** (1.678 g) and 5-[(4-fluorophenyl)sulfonyl]-2-fluorobenzoic acid **3** (2.000 g) in 1,1-dioxothiolane (20 ml) were added sodium carbonate (1.17 g) and chlorobenzene (20 ml) and slowly heated to 190°C. Water was removed by azeotropic distillation with chlorobenzene. Polycondensation occurred at 190°C and 250 mbar. After 10 h the resulting light-brown solution was stirred with water (50 ml) to dissolve the carboxylated poly(ether sulfone). For purification the polymer solution was dialyzed in water. Removal of the water by freeze drying results in the solid sodium salt of the carboxylated poly(ether sulfone). Yield 1.66 g (47%).

The free acid was obtained by neutralization of an aqueous solution of the above-mentioned salt with hydrochloric acid. Carboxylated poly(ether sulfone) precipitates as a voluminous mass which is difficult to filtrate.

GPC in DMAc: $M_n = 4200$, $M_w = 4900$, $Q = 1.17$.

^{1}H and ^{13}C NMR data cf. Tables 1 and 2. The degree of substitution (DS) was calculated from ^{1}H NMR data: $DS_{H\ NMR} = 0.27$ and from ^{13}C NMR data: $DS_{C\ NMR} = 0.24$. (The theoretical DS value is 0.5.) The M_n was calculated from ^{1}H NMR data: $M_n = 6900$.

Table 1
^{1}H NMR spectroscopic data of the carboxylated poly(ether sulfone) **5**

δ (ppm)	Multiplicity	J (Hz)	Assignment
8.30	d	2.3	H-7
8.17	dd	8.3/3.8	H-32
8.03; 8.02	d; d	8.7; n.d.	H-14; 22; 34
7.98; 7.96	d; d	8.7; 7.9	H-17; 26
7.82	d	8.3	H-9; 29
7.77	dd	9.1/2.6	H-5
7.45–7.20	m	–	H-10; 13; 21; 30; 35
7.00	d	8.3	H-18; 25
6.85	d	8.7	H-4

2.4.2. Poly(ether ether sulfone) from 2.5-dihydroxybenzoic acid and bis(4-fluorophenyl)sulfone 7

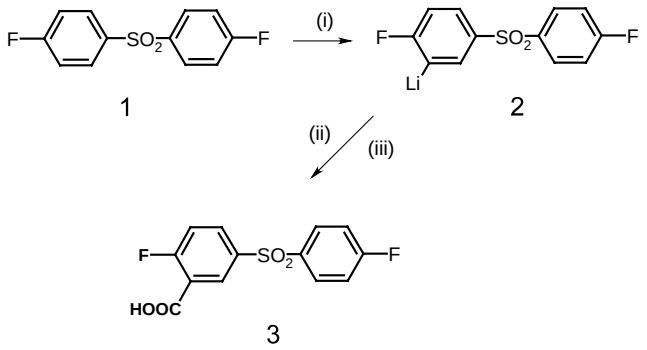
To a solution of 2.5-dihydroxybenzoic acid **6** (2.312 g, 1.500×10^{-2} mol) in 1,1-dioxothiolane (30 ml) were added sodium carbonate (2.65 g, 2.50×10^{-2} mol), chlorobenzene (30 ml) and water (5 ml) and slowly heated to 160°C. Water was removed by azeotropic distillation with chlorobenzene. To the dry solution bis(4-fluorophenyl)sulfone **1** (3.814 g, 1.500×10^{-2} mol) was added and the mixture was heated to 205°C at 250 mbar. After 10 h the product was added to diluted hydrochloric acid. A white precipitate was isolated and dried at 100°C and 10 mbar. The product was identified as not-carboxylated poly(ether ether sulfone) **7**. Yield 4.22 g (86.8%).

3. Results and discussion

In the literature two strategies are employed for the

Table 2
^{13}C NMR spectroscopic data of the carboxylated poly(ether sulfone) **5**

δ (ppm)	Assignment	δ (ppm)	Crosspeak 2D-^{1}H – ^{13}C	Assignment
170.06	C-1	131.31	H-5	C-5
169.21	C-3	130.46	–	C-6
162.43	C-19; C-24	130.09	H-7; H-14; H-22	C-7; C-14; C-22; C-34
159.53; 159.30	C-11; C-31; C-36	129.79	H-9; H-29	C-9; C-29
		129.58	H-17 or H-26	C-17; C-26
158.73; 158.54	C-12; C-20	129.39	H-17 or H-26	
		126.56	–	C-2
138.39; 137.95	C-16; C-27	119.84		
		119.63	H-10; H-13; H-21; H-30	C-10; C-13; C-21; C-30;
		119.34		C-35
136.60; 136.36	C-8; C-15; C-23; C-28; C-33	118.09	H-4	C-4
		116.22	H-25; H-18	C-18; C-25



Scheme 1. Synthesis of 5-[(4-fluorophenyl)sulfonyl]-2-fluorobenzoic acid (**3**). (i) *n*-BuLi/THF, $T = -78$°C; (ii) CO_2; (iii) aq. HCl.

synthesis of carboxylated poly(arylene ether sulfone)s. One is based on polymer analogous reactions the other one starts with modified monomers for the polycondensation polymerization. For the preparation of carboxylated Victrex® **VI** we used 5-[(4-fluorophenyl)-sulfonyl]-2-fluorobenzoic acid and bis(4-hydroxyphenyl)sulfone as monomers. We have chosen to introduce the electron withdrawing carboxy group in the bis(fluorophenyl)sulfone moiety to enhance the nucleophilic substitution of fluoride ions with bis(4-oxyphenyl)sulfone as the nucleophile.

3.1. Monomer synthesis

5-[(4-Fluorophenyl)sulfonyl]-2-fluorobenzoic acid **3** was prepared from bis(4-fluorphenyl) sulfone **1** by lithiation with BuLi followed by treatment with carbon dioxide (Scheme 1). In order to obtain a monocarboxylated monomer (free of dicarboxylated product) bis(4-fluorophenyl)sulfone **1** was treated first with BuLi in a molar ratio of 1:0.25 and then with carbon dioxide. The NMR data suggest the formation of 5-[(4-fluorophenyl)sulfonyl]-2-fluorobenzoic acid **3**. This result is supported by the HETCOR-spectrum (Fig. 1) where all the resonances were assigned to the corresponding hydrogen and carbon atoms.

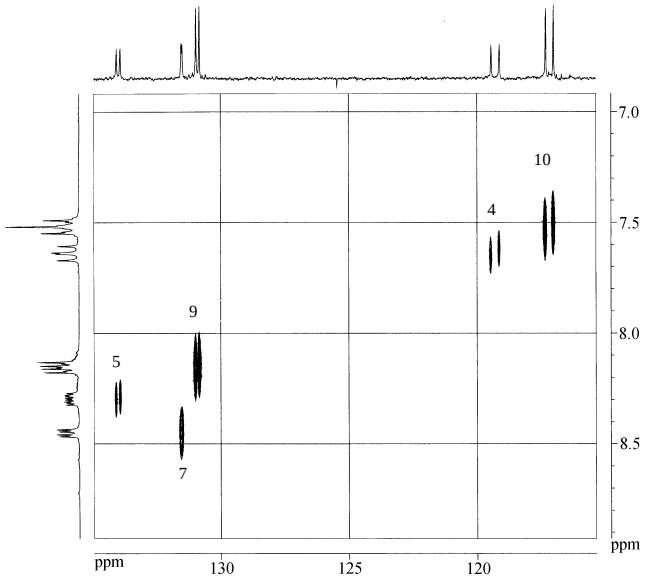
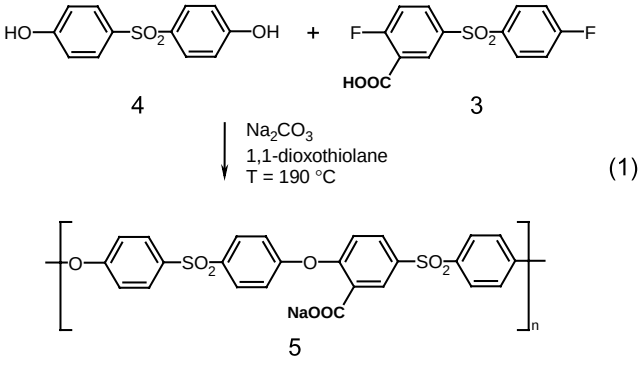


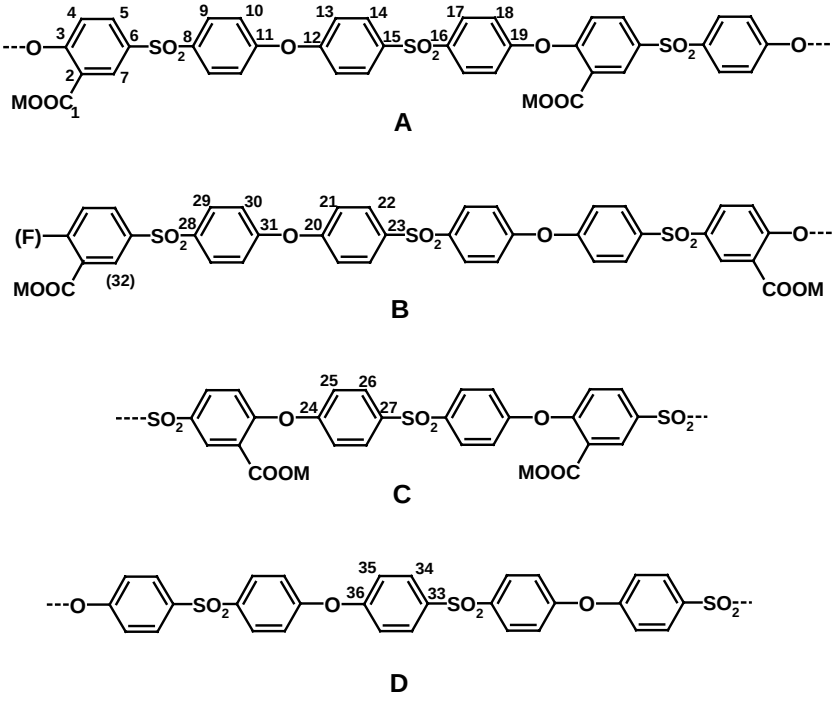
Fig. 1. HETCOR-spectrum of 2-[(4-fluorophenyl)sulfonyl]-5-fluorobenzoic acid **3** (solvent: DMSO-d_6).

3.2. Polycondensation

The polycondensation of the difluoro carboxylic acid **3** with bis(4-hydroxyphenyl)sulfone **4** was performed according to the general procedure for the preparation of poly(ether sulfone)s in 1,1-dioxothiolane solution at 190°C and 250 mbar in the presence of sodium carbonate (Eq. (1)). The product was purified by means of dialysis and was obtained in a yield of 47%. GPC analysis of the purified polymer reveals $M_n = 4200$ (with respect to polystyrene standards) and a polydispersity index $Q = M_w/M_n = 1.17$. The IR-spectrum of the polymer shows a typical spectrum of a poly(ether sulfone); a characteristic carbonyl absorption band at 1688 cm^{-1} reveals the presence of carboxylic acid groups.



The ^1H and ^{13}C NMR spectra (Figs. 2 and 3) obtained for the carboxylated polymer **5** are very complex due to two phenomena: From a theoretical point of view polycondensation of the symmetrical monomer **4** with the unsymmetrical monomer **3** results in three types of **3**–**4**–**3** based sequences (triads) **A**, **B**, and **C**. In addition due to decarboxylation the non-carboxylated sequence **D** is generated. The chemically not equivalent H and C atoms in the sequences **A**, **B**, **C**, and **D** were identified and assigned using the HETCOR-spectrum and for comparison the spectrum of unsubstituted poly(ether sulfone) (for the assignment cf. Section 2, Tables 1 and 2).



In the ^{1}H NMR spectrum of the polymer (Fig. 2) the resonance lines at $\delta = 8.30$ (H-7), 7.77 (H-5), and 6.85 (H-4) ppm for the carboxylated phenyl ring are readily detected. Evaluating the ratio (z) of the peak area (integral) of the resonance line corresponding to H-7 and the peak areas of the signals corresponding to the other aromatic hydrogen atoms the degree of substitution (DS in mol%) was calculated according to $DS = 8z/(1 - 6z)$. The degree of substitution obtained from ^{1}H NMR analysis ($DS_{exp} = 0.274$) is by 45% lower than theoretically expected ($DS_{th} = 0.5$). An explanation for this result is the occurrence of decarboxylation during polycondensation.

The complex resonance centered at $\delta = 8.17$ ppm (H-32) was assigned to the *ortho*-sulfonyl and the *ortho* carboxy proton of the terminal phenyl group. This signal was used to calculate the number average molecular weight of the polymer. A value of $M_n = 7400$ was found.

In order to obtain information on whether this route to carboxylated poly(ether sulfone)s can be applied also to poly(ether ether sulfone)s an analogous synthesis was performed starting with hydroquinone carboxylic acid **6** and bis(4-fluorophenyl)sulfone **1** (Eq. (2)). The polymer obtained, however, is a not carboxylated poly(ether ether sulfone) **7**. The polycondensation is obviously associated

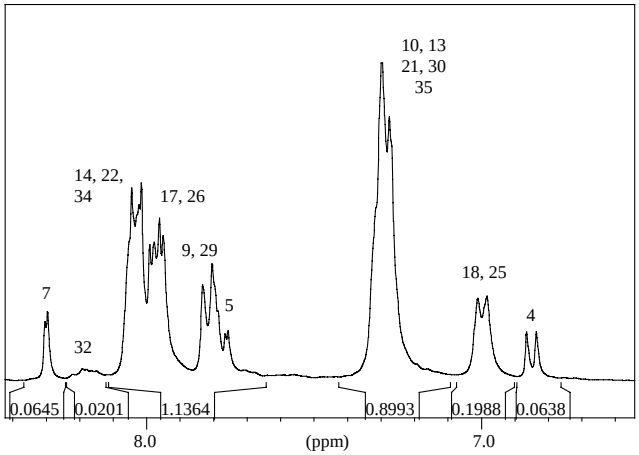


Fig. 2. ^{1}H NMR spectrum of carboxylated poly(ether sulfone) **5** (solvent: DMSO-d_6).

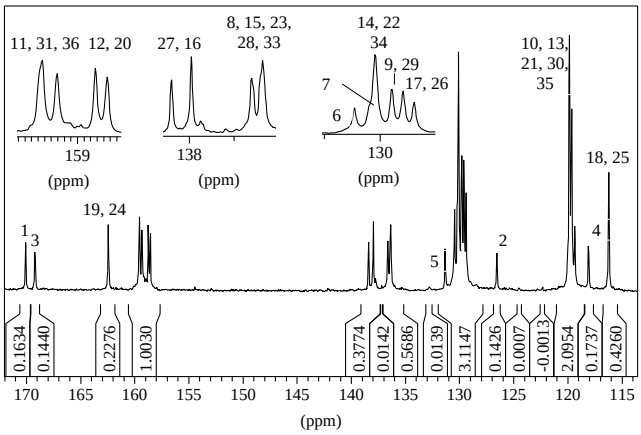
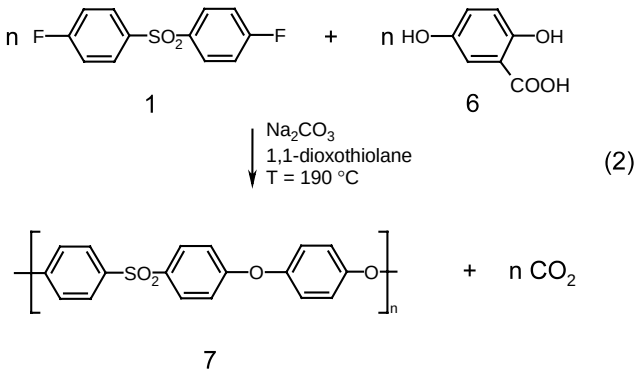


Fig. 3. ^{13}C NMR spectrum of carboxylated poly(ether sulfone) **5** (solvent: DMSO-d_6).

with a complete decarboxylation of either the monomer or the polymer.



4. Conclusions

The preparation of carboxylated poly(ether sulfone)s was accomplished starting from carboxylated monomers. The polycondensation polymerization, however, must be optimized in order to reduce the degree of decarboxylation and to increase the molecular weights.

Acknowledgements

Financial support of the Bundesministerium für Bildung und Forschung (Proj. Nr. 03N4001) and the Fonds der Chemischen Industrie is acknowledged.

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