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New Polymer Syntheses. 58. Alkylation of Aromatic Poly(pyridine ether)s and Their Application as Membranes

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ABSTRACT: The alkylation of aromatic poly(pyridine ether)s is sterically hindered, so that diethyl sulfate and γ-propanesultone are ineffective. After optimization of the reaction conditions, several poly(pyridine ether)s and poly(pyridine ether sulfone)s were almost quantitatively methylated with dimethyl sulfate in nitrobenzene. The isolated ionomers were characterized by elemental analyses, inherent viscosities, DSC measurements, and ^{1}H NMR spectra. In one case ^{15}N NMR spectra were measured in several solvents. WAXS powder patterns and DSC measurements indicate that most methylated poly(pyridinium ether)s are amorphous materials with higher glass-transition temperatures than those of the parent polyethers. The solubilities of all poly(pyridinium ether)s were studied in six different solvents. In the case of one methylated poly(pyridine ether sulfone), a membrane was prepared and gas separation was studied. High selectivities were found for CO_2/CH_4 and He/N_2.

Introduction

Aromatic polyethers, in particular poly(ether sulfone)s, are widely used as membranes for reverse osmosis and, mainly in bilayer structures, also for gas separation. In order to vary permeability and selectivity, various attempts have been made to modify the chemical structure of poly(ether sulfones) and poly(ether ketones). The introduction of anionic groups by sulfonylation is by far the most widely used method.[1-11]

The present work deals with an alternative approach which consists of two steps. The first step is the synthesis of copolyethers containing nitrogen heterocycles such as pyridine, pyrazine, and pyridazine rings. The second step is the alkylation of these heterocycles and, thus, the introduction of positive charges into the polymer backbone. Whereas synthesis and alkylation of polyethers derived from pyrazine will be described in a future part of this series,[12] the present paper deals with the methylation of poly(pyridine ether)s. Syntheses and characterization of the poly(pyridine ether)s have been described previously.[13,14]

Experimental Section

Materials. Dimethyl sulfate, a gift of Bayer AG (4150-Krefeld-Uerdingen), was used after distillation. Methyl triflate, methyl methanesulfonate, methyl iodide, diethyl sulfate, and γ-propanesultone were purchased from Aldrich Chemical Co. (7924 Steinheim, FRG). These reagents were used without further purification. The poly(pyridine ether)s used for the preparation of **2a–e**, **3**, and **4a–c** were those samples described in ref 13. The poly(pyridine ether sulfone)s used for the preparation of **4d** and **4e** were the samples described in ref 14.

Kinetic Studies of Methylation. A poly(pyridine ether) (0.5 mmol) was weighed into a 5-mm-o.d. sample tube and dissolved in 0.6 mL of nitrobenzene-d_5. A solution of the alkylating reagent (0.55 mmol) in 0.4 mL of nitrobenzene-d_5 was then added, the reaction mixture was thermostated at 20, 80, or 140 °C, and ^{1}H NMR spectra were recorded from time to time (see Table I).

Preparative Methylation of Poly(pyridine ether)s. A poly(pyridine ether) (10 mmol) was dissolved in 30 mL of dry nitrobenzene (distilled over P_4O_{10}) and heated with the dimethyl sulfate (12 mmol) 6 h to 80 °C. Afterward the reaction mixture was poured into ethyl acetate, and the precipitated polymer was isolated by filtration. The crude product was dissolved in methanol or dichloromethane, precipitated into diethyl ether, and dried at 80 °C in vacuo.

Preparation of Films for Gas Measurements. A 2 wt % solution of the polymer in dry dichloromethane was prepared. The solution was filtered, and then 10 or 20 mL of the solution was cast into a glass circle on a planar glass plate. In order to ensure complete evaporation of the solvent, the film was cured at room temperature overnight. The thickness of the resulting film was measured with a micrometer.

Gas Permeation Measurements.[15] The gas permeation measurements were carried out by the so-called "pressure-increasing method". The test cell and the calibrated volume were thermostated in a container controlled at ±0.1 °C. The gas pressure on the upstream face of the membrane was essentially atmospheric pressure during the experiments. The downstream pressure was kept at <2% of the upstream pressure and recorded as a function of time. The gas permeability was determined by the following equation:

$$P = \frac{ql}{(p_2 - p_1)At}$$

where P = gas permeability (m^3 m/m^2 s Pa), q/t = volume flow rate of gas permeate (m^3/s), l = membrane thickness (m), $p_2 - p_1$ = pressure difference across the membrane (Pa) and A = effective membrane area, here 0.00132 m^2. The ideal selectivity, α, is defined as the ratio of the pure component permeabilities:

$$\alpha = p_i/p_j$$

Measurements. The inherent viscosities were measured with an automated Ubbelode viscometer thermostated at 25 °C. The ^{1}H NMR spectra were recorded with a Bruker AC-100 FT-NMR spectrometer. Internal TMS served for shift referencing. The 35.4-MHz ^{15}N NMR spectra were obtained with a Bruker MSL-300 FT-NMR spectrometer in 20-mm-o.d. sample tubes equipped with a 4-mm-o.d. coaxial tube containing an $^{15}NH_4{}^{15}NO_3$ solution in D_2O. The DSC measurements were conducted with a Perkin-Elmer DSC-4 in aluminum pans at a heating rate of 20 °C/min.

Results and Discussion

Alkylation of Poly(pyridine ether)s. In order to optimize the reaction conditions required for a nearly

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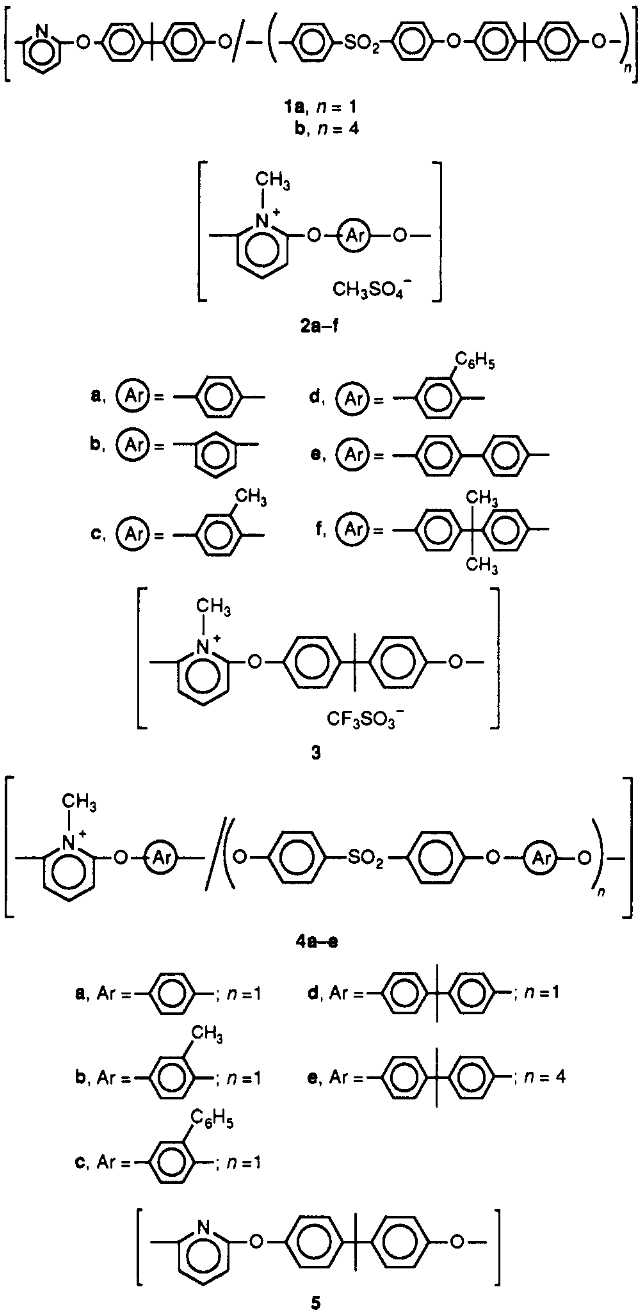
Table I
Methylation of Poly(pyridine ether) 1a in Nitrobenzene-d_5: Influence of Reaction Time and Temperature on the Conversion

time, h	dimethyl sulfate			methyl methanesulfonate		methyl iodide	
	20 °C	80 °C	100 °C	80 °C	140 °C	80 °C	140 °C
2	0	25	74	0	5	0	0
4	0	34	89	5	30	0	0
8	0	42	100	27	65	3	5
24	18	55	100	86	100	5	15
48	25	66	100	100	100	5	30

quantitative alkylation of the poly(pyridine ether)s, numerous alkylations were conducted in small quantities directly in 5-mm-o.d. NMR tubes and monitored by ^{1}H NMR spectroscopy. The poly(pyridine ether sulfone) **1a** (Chart I) proved to be advantageous for this screening process, because the methyl groups of Bisphenol-A can serve as an internal standard for the quantification of the alkylation reaction. Furthermore, the alkylated poly(pyridine ether sulfone) showed a good solubility in nitrobenzene and some other organic solvents. Five solvents were used (in deuterated form) as reaction media: chloroform, acetonitrile, dimethyl sulfoxide, dimethylformamide, and nitrobenzene. Chloroform turned out to be unfavorable either because all alkylations were too slow or because the partially methylated polyethers precipitated from this solvent. Dimethyl sulfoxide, dimethylformamide, and acetonitrile reacted with the stronger alkylating reagents, and, thus, only nitrobenzene proved to be useful for broader kinetic or preparative studies. Alkylations of **1a** in nitrobenzene were then conducted with six alkylating reagents: methyl triflate, methyl methanesulfonate, dimethyl sulfate, methyl iodide, diethyl sulfate, and γ-propanesultone. A 10% molar excess of these reagents was used for all spectroscopic studies, and the reaction temperature was varied between 20, 80, and 140 °C. ^{1}H NMR spectroscopy revealed that with diethyl sulfate and γ-propanesultone the conversions remained below 10% even at 140 °C. On the other hand, methyl triflate enabled a quantitative methylation even at room temperature within 1–2 h (depending on the concentration). The results obtained with methyl methanesulfonate, dimethyl sulfate, and methyl iodide are summarized in Table I. All results together allow two obvious conclusions: (1) The alkylation of poly(pyridine ether)s is sterically hindered by the substitution in the 2,6-position. (2) The reactivity of the alkylating reagents decreases in the order methyl triflate > dimethyl sulfate > methyl methanesulfonate > methyl iodide > γ-propanesultone. This order represents the electrophilicity of the reacting carbon and the stability of the leaving ion and is in agreement with various alkylation reactions known in organic chemistry.

Since dimethyl sulfate is the only commercially produced methylating reagent, it was preferentially used for preparative purposes. The methylated poly(pyridine ether)s prepared with this reagent (20% molar excess) in nitrobenzene at 80 °C have the formulas **2a–f**. One poly(pyridinium ether), **3**, was obtained at 20 °C by means of methyl triflate. Yields and properties of these ionomers are summarized in Table II. In addition to these homopolymers, five copolyethers containing diphenyl sulfone units were alkylated with dimethyl sulfate (**4a–e**). Their yields and properties are listed in Table III.

Chart I



Characterization of Methylated Poly(pyridine ether)s. The elemental analyses demonstrate by relatively high C and N values combined with low S values that the methylation was rather incomplete in the case of **2a** (20–25% conversion) and **2e** (75–80% conversion); in all other cases the degree of methylation was above 90%. These conclusions are confirmed by ^{1}H NMR spectra (Figures 1 and 2). In the case of **2a** and **2e**, precipitation of the partially methylated polyethers from the reaction mixture is responsible for the relatively low conversions. DSC measurements (see below) confirmed that **2a** and **2e** are crystalline, in contrast to all other methylated poly(pyridine ether)s. Incomplete methylation (80–90% conversion) was also found for the poly(pyridine ether sulfone)s **4a** and **4b**. Despite improved solubility (Table III), a small fraction of the polyethers precipitated from the reaction mixture. Here it must be taken into account that the poly(pyridine ether sulfone)s are random copolymers and may possess a certain degree of chemical heterogeneity. This means individual chains may be richer or poorer in pyridine units than the average, and chains richer in pyridine units tend to precipitate after partial methylation as demonstrated by **2a**.

Table II
Yields and Properties of Methylated Poly(pyridine ether)s

polymer	yield, %	η_{inh},[a] dL/g	elem form (form wt)		elem anal. % C	‰ H	% N	% S	T_g,[b] °C	T_g,[b,c] °C
2a	72	0.20	$C_{13}H_{13}NO_6S$	calcd	50.13	4.22	4.50	10.30	140	100
			(311.20)	found	64.10	4.11	7.06	2.50		
2b	78	0.20	$C_{13}H_{13}NO_6S$	calcd	50.13	4.22	4.50	10.30	133	82
			(311.20)	found	50.60	4.04	4.90	9.63		
2c	83	0.28	$C_{14}H_{15}NO_6S$	calcd	51.66	4.66	4.30	9.86	144	89
			(325.22)	found	53.91	4.65	4.84	7.77		
2d	34	0.53	$C_{19}H_{17}NO_6S$	calcd	58.88	4.43	3.62	8.28	185	115
			(387.24)	found	59.20	4.36	3.53	7.87		
2e	75	0.24	$C_{19}H_{17}NO_6S$	calcd	58.88	4.43	3.62	8.26	204	119
			(387.24)	found	63.21	4.40	3.88	6.37		
2f	81	0.30	$C_{22}H_{23}NO_6S$	calcd	61.49	5.41		7.46	173	107
			(429.30)	found	60.01	5.35	3.34	7.41		
3	85	0.28	$C_{20}H_{20}F_3NO_6S$	calcd	52.26	4.39	3.05	6.98	173	107
			(459.27)	found	53.22	4.33	3.10	6.70		

[a] Measured at 25 °C with $c = 2$ g/L in CH_2Cl_2/CF_3CO_2H (4:1 by volume). [b] From DSC measurements with a heating rate of 20 °C/min. [c] The values of the parent (non-methylated) poly(pyridine ether)s.

Table III
Yields and Properties of Methylated Poly(pyridine ether sulfone)s

polymer	yield, %	η_{inh}, dL/g	elem form (form wt)		elem anal. % C	% H	% N	% S	T_g,[d] °C	T_g,[d,e] °C
4a	65	0.38[a]	$C_{29}H_{25}NO_{10}S_2$	calcd	56.92	4.13	2.29	10.49	147	131
			(611.37)	found	61.20	4.03	2.43	8.65		
4b	74	0.60[a]	$C_{31}H_{29}NO_{10}S_2$	calcd	58.18	4.58	2.19	10.03	178	138
			(639.41)	found	62.30	4.48	2.26	8.54		
4c	81	1.15[a]	$C_{41}H_{33}NO_{10}S_2$	calcd	64.44	4.36	1.83	8.39	181	147
			(763.46)	found	65.50	4.19	1.91	8.00		
4d	91	0.88[b]	$C_{49}H_{45}NO_{10}S_2$	calcd	67.78	5.24	1.61	7.39	188	137
			(869.42)	found	65.03	4.98	1.58	7.61		
4e	75	0.46[c]	$C_{128}H_{111}NO_{24}S_5$	calcd	69.61	5.08	0.64	7.25	181	155
			(2206.42)	found	68.38	5.07	0.65	7.28		

[a] Measured at 25 °C with $c = 2$ g/L in CH_2Cl_2/CF_3CO_2H (4:1 by volume). [b] Measured at 25 °C with $c = 2$ g/L in CH_2Cl_2/C_2H_5OH (1:1 by volume). [c] Measured at 25 °C with $c = 2$ g/L in pure CH_2Cl_2. [d] From DSC Measurements with a heating rate of 20 °C/min. [e] The values of the parent (non-methylated) polyethers.[11,12]

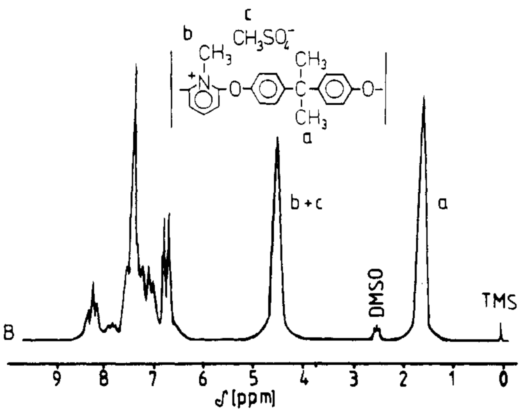


Figure 1. 100-MHz ^1H NMR spectrum of the methylated poly(pyridine ether) 2f measured in DMSO-d_6.

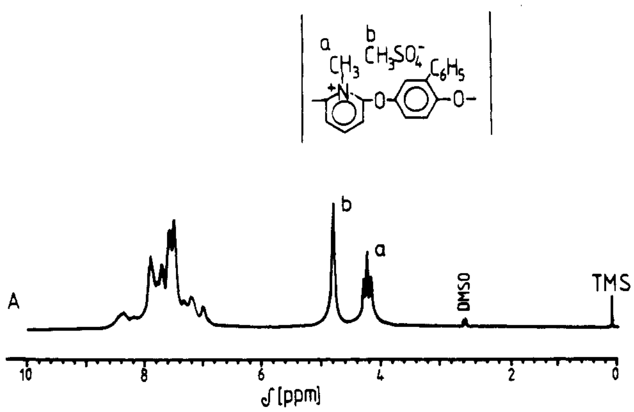


Figure 2. 100-MHz ^1H NMR spectrum of the methylated poly(pyridine ether) 2d measured in DMSO-d_6.

Concerning the NMR spectroscopic characterization of 2a–f and 4a–e, it should be mentioned that N^+CH_3 and $CH_3OSO_3^-$ protons formed in most cases on broad ^1H NMR signal in the range of 4.1–4.4 ppm when measured in DMSO-d_6 (Figure 1). A clear-cut separation was only observed for 2d (Figure 2). In this case the triplet pattern of the NCH_3 signal results from constitutional sequences of the phenyl substituents. In the case of 2f and its parent polyether 5, natural-abundance ^{15}N NMR spectra were measured in six different solvents. The δ values listed in Table IV indicate that both protonation (e.g., in CF_3CO_2H) and methylation cause an upfield shift of the ^{15}N signal by approximately 80 ppm. Such a strong upfield shift is also typical for low molecular weight pyridine derivatives.[16] Unfortunately, the low sensitivity of the natural-abundance ^{15}N NMR measurements does not allow one to monitor the methylation of poly(pyridine ether)s (5) quantitatively.

Even though the methylation of the poly(pyridine ether)s should not affect the aromatic ether group, attempts were made to prove or disprove the absence of degradation reactions. Unfortunately, it is difficult to elucidate this problem for two reasons. First, a comparison of number-average molecular weights by means of colligative methods is not feasible, due to the dissociation of the counterions. Second, methylated and non-methylated poly(pyridine ether)s will have different hydrodynamic volumes, due to the polyelectrolyte effect of the methylated species. Nonetheless, viscosity measurements of 1a, 1b, 4d, and 4e were conducted in the same solvent (DMF).

Table IV
^{15}N NMR Chemical Shifts δ (in ppm Relative to External NO_3^-) of a Methylated and Non-methylated Poly(pyridine ether)

	chem shift					
polymer	THF	$CHCl_3$	DMSO	CH_3OH	HCO_2H	TFA
5	-129.1	-130.4			-189.0	-214.6
2f	insol	insol	-206.1	-207.7	-208.5	-210.5

Table V
Solubilities of Methylated Poly(pyridine ether)s in Various Solvents

	solubility determined at 20 °C in					
polymer	H_2O	CH_3OH	CH_2Cl_2/ C_2H_5OH[a]	CH_2Cl_2/ TFA[b]	CH_2Cl_2	DMSO
2a	–	–	–	–	–	–
2b	–	+	+	+	–	+
2c	–	+	+	+	–	+
2d	–	+	+	+	–	+
2e	–	–	–	–	–	–
2f	G[d]	+	+	+	–	+
3	–	+	+	+	–	+
4a	–	+	–	+	–	+
4b	–	+	–	+	–	+
4c	G[d]	+	+	+	–	+
4d	G[d]	+	+	+	–	+
4e	–	–	+	+	+	+

[a] Volume ratio 1:1. [b] Volume ratio 4:1. [c] Soluble upon heating. [d] Gelation.

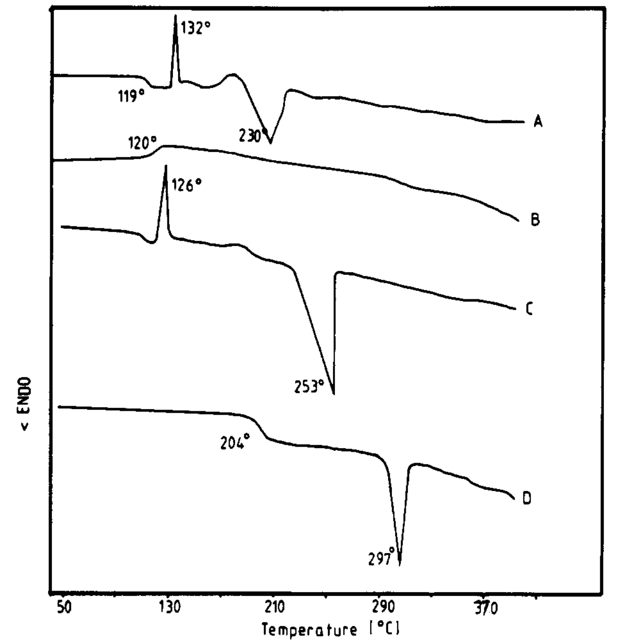


Figure 3. DSC measurements conducted at a heating (cooling) rate of 20 °C/min. (A–C) Polyether prepared from 4,4′-dihydroxybiphenyl and 2,6-difluoropyridine:[14] (A) first heating; (B) first cooling; (C) second heating; (D) methylated poly(pyridine ether) **2e**, first heating.

Inherent viscosities of 0.45 and 0.56 dL/g were found for **1a** and **1b**, respectively. Viscosity values of 1.0 and 1.2 dL/g were obtained for **4d** and **4e**, respectively. The significantly higher viscosities of the methylated polyethers suggest that degradation was weak or absent. This conclusion is supported by light scattering measurements of **1b** and **4e** in DMF. A weight-average molecular weight (M_w) of 220 000 was found for **1b**,[14] and a M_w value of 180 000 was found for **4e**.

Table VI
Permeabilities and Selectivities of Membranes Prepared from the Methylated Poly(pyridine ether sulfone) 4e and Its Parent Polyether 6

	permeability[a] of			
polymer	CO_2	CH_4	He	N_2
4e	42.00	1.05	91.35	1.10
6	72.25	29.65	86.90	23.00

	selectivity of			
	CO_2/CH_4	CO_2/N_2	CH_4/N_2	He/N_2
4e	39.9	37.8	0.9	82.3
6	2.4	3.1	1.3	3.8

[a] Dimension: 10^{-18} $m^3/m/m^2$ s Pa.

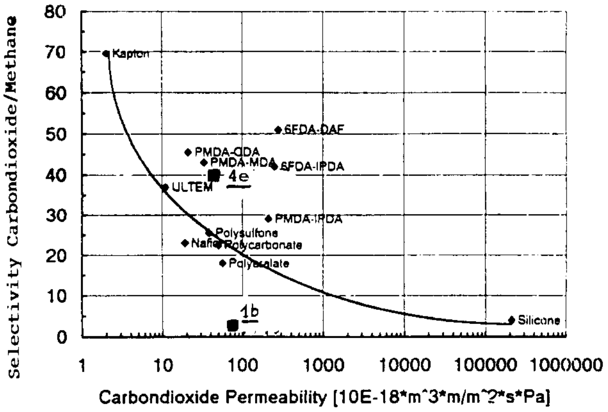


Figure 4. Comparison of selectivity and permeability of the poly(methylpyridinium ether sulfone) **4e** and its parent polyether **1b** with various commercial membrane materials.

The solubilities of all methylated poly(pyridine ether)s were studied in six different solvents. The results listed in Table V show some interesting structure–property relationships. The partially methylated, crystalline polyethers **2a** and **2e** are insoluble in all solvents under investigation. All other poly(pyridinium salts) were soluble in DMSO and mixtures of CH_2Cl_2 and trifluoroacetic acid. No polymer was completely soluble in hot water, and only one ionomer, **4e**, is soluble in pure CH_2Cl_2. In this case the high content of poly(ether sulfone) units improved the solubility in nonprotic organic solvents and eliminated the solubility or swellability in water or methanol. This aspect is of interest for a potential application as membrane.

Finally, the DSC measurements need a short discussion. Strong endotherms indicating a melting process were only observed for the ionomers **2a** and **2e** (Figure 3). In both cases WAXS powder patterns confirmed the existence of a crystalline phase. In all other cases the DSC heating curves only revealed glass-transition steps, indicating a completely amorphous character of the samples. A comparison of the glass-transition temperatures (T_g's) with those of the parent poly(pyridine ether)s (Tables II and III) demonstrates that the methylation strongly reduces the segmental mobility. Despite incomplete conversion, this difference approaches 80 °C for polymer **2e**. In this case the methylation also raises the melting point as demonstrated in Figure 3. The influence of the counterion on T_g and crystallinity is an interesting question which will be studied in the future.

Gas Separation Measurements. In order to obtain some preliminary information on the usefulness of poly(pyridine ether)s and their *N*-methyl derivatives as membranes, several attempts were made to prepare self-supporting membranes from the following pairs of polyesters: **2f**/**5**, **1a**/**4d**, and **1b**/**4e**. However, in the case of **2d** the molecular weight was too low. The films cast from CH_2Cl_2/CH_3OH solutions were porous and brittle. Also in the case of **4d** the film was turbid and brittle. Apparently the high concentration of ionic groups results in the formation of a biphasic system with one phase rich in ions and a second phase poor in ions (the WAXS powder pattern did not show a significant degree of crystallinity). However, tough transparent films could be cast from solutions of **1b** and **4e**.

The films of **4e** and **1b** were exposed to several gases under increasing pressure, and both permeability and selectivity were measured. The results summarized in Table VI show that the selectivity of **4e** toward mixtures of several gases is in all cases higher than that of **1b**. Particularly high selectivities were found for CO_4/CH_4 and He/N_2. Figure 4 illustrates a comparison with commercial membranes tested under identical conditions with regard to the separation of CO_2 and CH_4. It is evident that the membrane of **4e** can compete with the best poly(ether imide) membranes (PMDA polymers in Figure 4). However, the mechanical properties of poly(ether imide)s suffer from plastification upon increasing pressure of CO_2 in contrast to the poly(ether sulfone)s. Therefore, these preliminary results suggest that poly(ether sulfone)s modified with *N*-methylpyridinium groups may be worthy of further evaluation as membrane materials.

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