Journal of Fluorine Chemistry, *59* (1992) 285–288

Preliminary Note

Synthesis and polymerization of *p*-pentamethyldisiloxanyl-α,β,β-trifluorostyrene and the oxygen permeability of the polymer

Toshiki Aoki, Jun Watanabe, Yoshiyuki Ishimoto, Eizo Oikawa
Department of Material and Chemical Engineering, Faculty of Engineering, Niigata University, Ikarashi 2-8050, Niigata, 950-21 (Japan)

Yoshio Hayakawa and Masakazu Nishida
Government Industrial Research Institute, Nagoya, Hirate-cho, Kita-ku, Nagoya 462 (Japan)

(Received October 14, 1991; accepted March 26, 1992)

Abstract

A novel monomer, *p*-pentamethyldisiloxanyl-α,β,β-trifluorostyrene, has been synthesized and polymerized to give a white polymer. Membranes obtained from the polymer exhibited an oxygen permeability coefficient (P_{O_2}: cc(STP) cm/cm^2 s cmHg) and an oxygen separation factor ($\alpha = P_{O_2}/P_{O_2}$) of 1.8×10^{-9} and 2.4, respectively. The P_{O_2} value is considerably higher than values for other poly(mono-substituted tetrafluoroethylenes). The introduction of a pentamethyldisiloxanylphenyl group into poly(tetrafluoroethylene) has been found to be very effective for the enhancement of P_{O_2} values.

The basic requirements for oxygen permselective membranes are a high oxygen permeability coefficient (P_{O_2}) and a high oxygen separation factor ($\alpha = P_{O_2}/P_{N_2}$). Since P_{O_2} is equal to the product of the oxygen solubility coefficient (S_{O_2}) and the oxygen diffusion coefficient (D_{O_2}), fluorine-containing polymers which have a high oxygen solubility are expected to show a high P_{O_2} value. In practice, however, the P_{O_2} value of fluorine-containing polymers is very low. This is probably due to their high crystallinity, the crystalline region prohibiting significantly permeation of oxygen molecules so that the D_{O_2} and S_{O_2} values are very low.

In order to increase the P_{O_2} values of fluorine-containing polymers to match their high S_{O_2} values we have prepared blend membranes of fluorine-containing polymers with siloxane-containing polymers [1, 2]. In this study, in order to increase P_{O_2} by decreasing the crystallinity and increasing S_{O_2},

0022-1139/92/$5.00

we have prepared a polymer with a main chain composed of poly (α,β,β-trifluorostyrene) and with oligosiloxane grafts, and estimated the oxygen permeability of the polymer obtained.

The novel monomer *p*-pentamethyldisiloxanyl-α,β,β-trifluorostyrene (**5a**) was synthesized according to the route depicted in Scheme 1. Using the same reaction as that in Scheme 1, *p*-chloropentamethyldisiloxane was obtained from *p*-bromochlorobenzene in a better yield (21.0%) than that for compound **3** (12.7%) but the corresponding Grignard reagent (**4a**) failed to form. In contrast, compound **3** gave **4a** in good conversion (93.7% estimated by GC methods).

The yield (7.9%) of **5a** was lower than that of **5c** (14.5%) and almost the same as that of **5b** (7.4%). These low yields are accounted for by the formation of by-products such as 1,2-diphenyldifluoroethene [3, 4]. However, yields via this route are almost the same as those from an alternative route [5] employing α,α,α-trifluoroacetophenone (the total yield was 17.5%), and furthermore the number of reaction steps in the present route is two, while the number in the alternative method was four. Hence, the present route is suitable for the synthesis of **5a**. The physical and spectroscopic data of the compounds thus prepared were as follows:

Compound **1**: B.p., 65 °C/1.0 mmHg. ^{1}H NMR (CCl_4, TMS) δ: 0.60 (s, 6H, $SiCH_3$); 7.30 (m, 4H, phenyl protons) ppm.

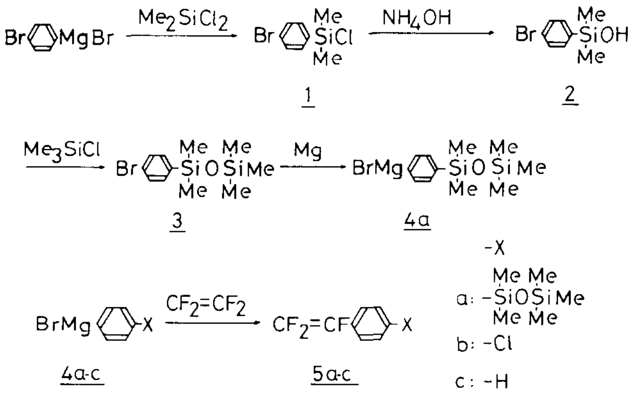
Compound **2**: ^{1}H NMR (CCl_4, TMS) δ: 0.33 (s, 6H, $SiCH_3$); 3.34 (s, 1H, OH); 7.30 (m, 4H, phenyl protons) ppm.

Compound **3**: B.p., 85 °C/2.0 mmHg. ^{1}H NMR (CCl_4, TMS) δ: 0.10 [s, 9H, $OSi(CH_3)_3$]; 0.33 [s, 6H, $Si(CH_3)_2O$]; 7.45 (m, 4H, phenyl protons) ppm.

Compound **5a**: $R_f = 0.65$ (eluent n-hexane using silica-gel chromatography). ^{1}H NMR (CCl_4, TMS) δ: 0.10 [s, 9H, $OSi(CH_3)_3$]; 0.33 [s, 6H, $Si(CH_3)_2O$]; 7.55 (m, 4H, phenyl protons) ppm. IR(NaCl) cm^{-1}: 1762 ($CF_2{=}CF$); 1572 ($CH{=}CH$); 1258 ($SiCH_3$); 1070 (SiO).

Compound **5b**: $R_f = 0.45$ (eluent $CHCl_3$ using silica-gel chromatography).

Compound **5c**: B.p., 46.0 °C/23 mmHg.



Scheme 1. Synthetic route to *p*-pentamethyldisiloxanyl-α,β,β-trifluorostyrene.

TABLE 1

Emulsion polymerization[a] of α,β,β-trifluorostyrene (**5c**) and its derivatives (**5a, b**)

Monomer[b]	Yield (%)	$\bar{M}_n$ ($\times 10^4$)[c]	$\bar{M}_n$ ($\times 10^4$)[c]	$\bar{M}_w/\bar{M}_n$[c]	Appearance
5a	14.3	23	6.9	3.3	white solid
5b	20	5.28	2.48	2.12	white solid
5c	95	57.5	30.9	1.86	white solid

[a] Using potassium persulfate as initiator and dodecylamine hydrochloride as emulsifier at 70 °C for 72 h.

[b] For numbering, see Scheme 1.

[c] Determined by GPC methods using THF as the eluent.

TABLE 2

Oxygen permeation behaviour of poly(p-pentamethyldisiloxanyl-α,β,β-trifluorostyrene) [poly(**5a**)] and other fluorine-, siloxane- or benzene ring-containing polymers

No.	Polymer	P_{O_2}[a]	α	D_{O_2}[b]	D_{O_2}/D_{N_2}	S_{O_2}[c]	S_{O_2}/S_{N_2}
1	*poly*(**5a**)	1.8	2.4	0.45	1.5	4.0	1.6
2	PTFE[d]	0.43	3.2	0.15	1.8	2.8	1.8
3	FEP[d]	0.49	3.1	0.18	1.9	2.7	1.6
4	PFA[d]	0.42	3.5	–	–	–	–
5	PCTFE[d]	0.004	–	–	–	–	–
6	PPDSS[e]	4.0	3.0	1.8	1.8	2.2	1.7
7	PS[e]	0.12	5.5	0.056	2.8	2.2	2.0
8	PDMS[e]	35.2	1.9	18.9	1.5	1.9	1.3

[a] In 10^{-9} cc(STP) cm/cm^2 s cmHg units.

[b] In 10^{-6} cm^2 s^{-1} units.

[c] In 10^{-3} cc(STP)/cm^3 cmHg units.

[d] Ref. 6: PTFE = poly(tetrafluoroethylene); FEP = copoly(tetrafluoroethylene/hexafluoropropylene); PFA = copoly(tetrafluoroethylene/heptafluoropropyl trifluorovinyl ether); PCTFE = poly(chlorotrifluoroethylene).

[e] Ref. 7: PPDSS = poly[p-(pentamethyldisiloxanyl)styrene]; PS = polystyrene; PDMS = poly(dimethylsiloxane).

Radical polymerizations of **5a–c** were carried out in a degassed ampoule using potassium persulfate as the initiator and dodecylamine hydrochloride as the emulsifier [5] (Table 1). Compounds **5a** and **5b** could be polymerized to give a high-molecular-weight polymer in a similar manner to the unsubstituted monomer, **5c**. However, the yields of poly(**5a**) and poly(**5b**) were much less than that of poly(**5c**). This may be explained by the formation of a cyclic dimer [5].

The resulting poly(**5a**) was a white solid, but incapable of forming a tough membrane because of contamination by the cyclic dimer (observed by GPC methods). For this reason, a laminated membrane composed of poly(**5a**) and crosslinked poly(dimethylsiloxane) was used for the measurement of the oxygen permeability (Yanaco, GTR-10), and the P_{O_2} value of poly(**5a**) was calculated using the series-model equation [1]. Table 2 lists the results and related data. The P_{O_2} value for poly(**5a**) (No. 1) is considerably higher than the values listed for poly(tetrafluoroethylene) and other poly(mono-substituted tetrafluoroethylenes) (Nos. 2–5). Introducing a pentamethyldisiloxanylphenyl group into the side-chains of poly(tetrafluoroethylene) increases the P_{O_2} value because of the increase in D_{O_2} (Nos. 1 and 2). This phenomenon may be attributed to the decrease in crystallinity and the enhanced mobility of the polymer chains. We have reported similar results for polystyrene [7] (Nos. 6 and 7). In addition, a high value of S_{O_2} for poly(**5a**) indicates that this factor contributes very significantly towards the high value for P_{O_2} for poly(**5a**).

References

1 T. Aoki, E. Oikawa, Y. Hayakawa and M. Nishida, *J. Membr. Sci.*, *57* (1991) 207.
2 Y. Kawakami, T. Aoki and Y. Yamashita, *Polym. Bull.*, *17* (1987) 293.
3 T. F. McGrath and R. Levine, *J. Am. Chem. Soc.*, *77* (1955) 4168.
4 S. Dixon, *J. Org. Chem.*, *21* (1956) 400.
5 R. B. Hodgdon Jr., *J. Polym. Sci.*, *A6* (1986) 171.
6 J. Brandup and E. H. Immergut, *Polymer Handbook*, Wiley-Interscience, New York, 1989, Vol. VI, p. 440.
7 Y. Kawakami, H. Karasawa, H. Kamiya, T. Aoki and Y. Yamashita, *Polym. J.*, *18* (1986) 237.