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Preparation and properties of polyacetylene membranes substituted with trifluoromethylated heterocyclic groups

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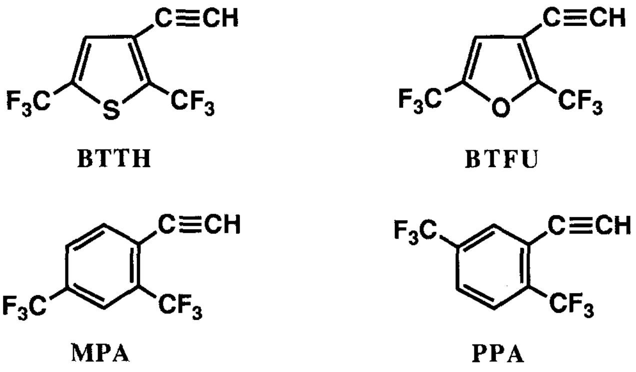
Summary

Membranes of poly[2,5-bis(trifluoromethyl)-3-ethynylthiophene] and poly[2,5-bis(trifluoromethyl)-3-ethynylfuran] were prepared and their properties were evaluated. They were found to be highly gas permeable, and showed somewhat low liquid permeability and preferential permeation of water in a pervaporation of aqueous alcohol.

Introduction

Recently substituted poly(acetylene)s containing heterocycles, such as thiophene and furan rings, have been synthesized and their electrical properties have been examined as potential organic conductors and chromatic materials.(1)

Since the films of substituted poly(acetylene)s with semi-rigid backbones of conjugated double bonds have shown relatively high gas permeability, they have been of interest as the materials of selective gas permeable membranes.(2-4) In order to get a tough film with self-supporting property for gas and liquid permeation, the molecular weight more than 10^5 would be required for poly(phenylacetylene)s.



BTTH BTFU

MPA PPA

Figure 1 Structures of Monomers

Although the molecular weights of poly(2-ethynylthiophene) and poly(3-ethynylthiophene) prepared by using the catalysts based on WCl_6 or $MoCl_5$ remained less than 2 x10^4, poly[2,5-bis(trifluoromethyl)-3-ethynylthiophene] (polyBTTH) gave a high molecular weight polymer.(5,6) Besides, the trifluoromethyl groups in the poly(phenylacetylene)s such as polyMPA and polyPPA (Figure 1) were found to be effective for improvement of gas permeability through their films.(7)

In this study, the membranes of polyBTTH and poly[2,5-bis(trifluoromethyl)-3-ethynylfuran] (polyBTFU) were prepared. Their gas and liquid permeabilities were evaluated and compared with those of substituted poly(phenylacetylene)s.

Results and Discussion

The results of polymerizations of BTTH and BTFU are shown in Table I. PolyBTTH and polyBTFU having high molecular weights were obtained in good yields. Their molecular weights were both intermediate between those of poly(3-ethynylthiophene) and poly(phenylacetylene)s such as polyMPA and polyPPA. In the polymerization of substituted acetylenes by catalysts of group 5 and 6 transition metals, the molecular weights of the polymers have been reported to depend on the bulkiness of substituents in the monomers.(8,9) The steric effect in the polymerization of BTTH and BTFU would be similar to those in phenylacetylenes with the trifluoromethyl groups at their ortho-positions. Though the inactivation of catalyst or propagating species by the hetero atoms may occur, the bulky trifluoromethyl groups around the hetero atoms of BTTH and BTFU possibly reduce their interactions.(5,10)

Table I Polymerization of Arylacetylenes by WCl_6-Ph_4Sn [a]

Monomer	$[M]_o$ (mol l^{-1})	Temp. (°C)	Time (h)	Yield (%)	$\overline{Mn}$ (10^5)
BTTH	0.50	30	24	96	3.3
BTFU	1.0	40	24	82	1.9
3-ethynylthiophene	0.50	30	24	89	0.10 [b]
MPA	0.67	40	24	100	13
PPA	0.68	40	24	96	5.2

[a] Polymerizations were carried out in Toluene.
$[WCl_6]_o = [Ph_4Sn]_o = 10$ mmol l^{-1}
[b] Determined by GPC correlated to standard polystyrene in THF.

Both polyBTTH and polyBTFU were reddish brown powders, whose absorption maxima were observed at 474 ($\varepsilon = 4.9 \times 10^3$) and 446 ($\varepsilon = 5.9 \times 10^3$) nm, respectively. These polymers were completely soluble in C_6F_6, *m*-

and p-$(CF_3)_2C_6H_4$ and $CF_2ClCFCl_2$(Freon 113), partially soluble in acetone and THF, and insoluble in n-hexane, chloroform and toluene. They had good film-forming property by the solution casting technique due to their high molecular weights. The membranes were a little brittle and occasionally ruptured under pressure and mechanical stress.

Table II shows the results of thermogravimetry of polyBTTH and polyBTFU. These polymers exhibited no decrease in weight up to 240°C. A distinct glass transition of the polymers could not be observed in the differential scanning calorimetry measurements. In polyBTFU, an exothermic peak existed at 190°C, which disappeared at the second heating after annealing at 200°C for 30 min.(1)

Surface characteristics of the polymer membranes were estimated by measuring contact angles of water and aqueous alcohol.(Table III) They had rather low surface tensions due to their high fluorine contents.

Table II Decomposition Temperature of Polymers

Polymer	Td(°C)	
	Air	N_2
polyBTTH	266	267
polyBTFU	291	305

Table III Contact Angles(θ) and Critical Surface Tensions(γ_c) [a]

Polymer	θ [b] (°)	γ_c (dyn/cm)
polyBTTH	100	22
polyBTFU	101	21

[a] Measured at 25°C

[b] Contact angle of distilled water

Gas Permeation

The gas permeabilities of polyBTTH and polyBTFU membranes were estimated for N_2, O_2, CO, CH_4, CO_2, and the results are shown in Table IV.

Both of the polymers had relatively high gas permeability compared with usual glassy polymers,(11) which may be due to their semi-rigid backbones and bulky substituents. Their oxygen permeability coefficients were lower than those of poly(phenylacetylene)s such as polyMPA and polyPPA. The permselectivities of polyBTTH and polyBTFU for oxygen to nitrogen were larger than those of poly(phenylacetylene)s, which were in accordance with the usual inverse relationship between selectivity and permeability.

Table IV Gas Permeability Coefficients of Poly(arylacetylene)s [a, b]

Polymer	P_{O_2}	P_{N_2}	P_{CO}	P_{CH_4}	P_{CO_2}
polyBTTH	7.2	2.2	2.3	1.2	18
polyBTFU	12	3.9	3.0	2.2	22
polyMPA	16	6.0	-	-	-
polyPPA	45	1.9	-	-	-

[a] Measured at 25°C

[b] In 10^{-9} $cm^3(STP)cm{\cdot}cm^{-2}sec^{-1}cmHg^{-1}$

Pervaporation

Table V summarizes the results of pervaporation measurements in 10 % aqueous ethanol solution through the membranes of polyBTTH and polyBTFU. They showed somewhat low permeabilities of water and ethanol, and preferential permeation of water despite of their high fluorine contents.(12-14) A compact structure and a marked hydrophobicity of the polymers would prevent them from swelling, resulting their low liquid permeability.

Table V Results of Pervaporation in 10% Aqueous Alcohol [a]

Polymer	R_{H_2O} [b]	R_{EtOH} [b]	α_{H_2O}
polyBTTH	21	0.17	14
polyBTFU	19	0.19	11

[a] Measured at 25°C

[b] In 10^{-5} $g{\cdot}m{\cdot}m^{-2}h^{-1}$

Pervaporation is controlled by the mass transport mechanism described in the solution-diffusion model.(15) The solubility of ethanol into the polyBTTH and polyBTFU membranes will be higher than that of water because of the marked hydrophobicity of the membranes. Therefore the preferential permeation of water is attributable to the higher diffusivity of water in the polymer matrix, which arises from its advantageous molecular dimension.(16)

Experimental

Materials

2,5-Bis(trifluoromethyl)furan(**1**) and 1,1-dichloro-2,2-difluoroethylene (**2**) were prepared as reported in the literature.(17,18)

2,5-Bis(trifluoromethyl)-3-(2,2-dichloro-1-fluorovinyl)furan(**3**) : to anhydrous etherial solution(100ml) of **1**(10.3g, 0.050mol) was added a hexane solution of n-butyl lithium(40ml, 0.063mol) over 10 min at -40°C ~ -30°C. The mixture was stirred for additional 5 h and then added to anhydrous etherial solution(30 ml) of **2**(26.0 g, 0.20 mol) at -60°C ~ -40°C over 30 min. After stirring for additional 90 min, the solution was acidified with dil HCl. The organic layer was washed with aq $NaHCO_3$ and dried over anhydrous Na_2SO_4. After evaporation of the solvents, the residue was distilled under reduced pressure to give **3**(7.1 g, 45% yield).

Compound **3** had bp 78 ~ 80°C/40 mmHg ; ^{1}H-NMR($CDCl_3$) : 7.21(s, 1H) ; ^{19}F-NMR : 9.56(d, 3F), 7.85(s, 3F), -23.65(q, 1F) ; MS(20eV) m/e(relative intensity) : 316(100)M^+, 297(13)$[M-F]^+$, 281(74)$[M-Cl]^+$; IR : 1620 cm^{-1} ($FC=CCl_2$).

2,5-Bis(trifluoromethyl)-3-ethynylfuran(BTFU) : to an etherial solution (100ml) of **3**(7.0 g, 0.022 mol) was added a hexane solution of n-butyl lithium(42 ml, 0.066 mol) at -60°C ~ -50°C over 15 min. After stirring for additional 3 h, the solution was acidified with dil HCl. The organic layer was washed with aq $NaHCO_3$, dried over anhydrous Na_2SO_4, and distilled to give BTFU(2.1 g, 42% yield).

BTFU had bp 99 ~ 100°C ; ^{1}H-NMR($CDCl_3$) : 3.32(s, 1H), 6.92(s, 1H) ; ^{19}F-NMR : 13.83(s, 3F), 15.20(s, 3F) ; MS m/e : 228(59)M^+, 209(22)$[M-F]^+$; IR : 3320($\equiv$C-H), 2140(C$\equiv$C).

Polymerization

Polymerizations were carried out under argon atmosphere according to the procedure described in a previous paper.(7)

Film Preparation

Polymer films used in permeability measurements were prepared by casting ca. 5 wt% C_6F_6 solutions of polymers on glass surface and allowing the solvent to evaporate at room temperature. The films were stripped from the glass surface by immersion in water and dried under vacuum at 40°C for 24 h.

Gas Permeation

The gas permeability of polymer films were estimated at 25°C by gas chromatography using air(O_2, N_2) and mixed gases(CO(10%), CH_4(27%), CO_2(7%), N_2(56%)), where the upstream pressure of the membranes were maintained atmospheric pressure and 113 cmHg respectively, and down stream ca.10^{-2} mmHg.

Pervaporation

A 10 wt% of aqueous ethanol solution was fed at the upside of the membrane and the downstream pressure was maintained at ca.10^{-1}mmHg. After the feed solution was supplied onto the membrane in the permeation cell, the membrane was allowed to stand overnight.

The composition and flux of permeate were estimated at 25°C by a gas chromatograph connected directly to the pervaporation cell. The permeation rate, R in $g{\cdot}m{\cdot}m^{-2}h^{-1}$, was calculated by correcting the flux for the thickness of the membrane. The separation factor, α, which was a measure of the preferential permeation component A, was defined as the concentration ratio Y_A/Y_B in the permeate divided by the concentration ratio X_A/X_B in the feed, where A and B indicate water and ethanol, respectively.

Instruments

IR spectra were taken with a JASCO IR-810 infrared spectrophotometer. UV-visible spectra of polymers in p-$(CF_3)_2C_6H_4$ were taken with a Hitachi 320 spectrophotometer. Mass spectra were obtained with a Shimadzu QP-1000 mass spectrometer. ^1H-NMR(90MHz) and ^{19}F-NMR(84.67MHz) measurements were recorded on a Hitachi R-90H instrument, and chemical shifts were defined as δ values relative to TMS and CF_3CO_2H, respectively. Molecular weights of polymers were determined by a Hewlett-Packard 502 high speed membrane osmometer using p-$(CF_3)_2C_6H_4$ as a solvent. Thermal analysis were performed with a Seiko I & E DSC-20 differential scanning calorimeter and TG-20 thermogravimeter at a heating rate of 10°C min^{-1}. Gas permeability of the films were measured with a Yanako GTR-10. Pervaporations were performed with a Yanako GTR-12L. Contact angles were measured with droplets of distilled water and aqueous alcohols on a Erma G-1 goniometer, and critical surface tensions were estimated by the Zisman plots.

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