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Gas and vapor permeability of perfluoroalkylated polymers

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Summary

Three polymers bearing benzene rings: polystyrene, poly(2,6-dimethyl-*p*-phenylene oxide) and poly(diphenylacetylene), were chemically modified with bis(heptafluorobutyryl) peroxide. The heptafluoropropylated products have higher gas permeabilities than the parent polymers. In the pervaporation of aqueous ethanol, modified poly(diphenylacetylene) showed ethanol permselectivity.

Introduction

Fluorine-containing polymers have water- and oil-repellency, high thermal stability, chemical and oxidative resistance, and a low refractive index. As they also show relatively high permeability in gas permeation and ethanol permselectivity in pervaporation of aqueous alcohol, polymers rich in fluorine are of interest for use as membranes in separation processes.[1,2]

Fluorination and perfluoroalkylation of preformed polymers are convenient methods for preparing fluoropolymers. Poly[1-(trimethylsilyl)propyne] film is directly fluorinated on exposure to fluorine, the resulting film having improved performance as a gas separation membrane.[3]

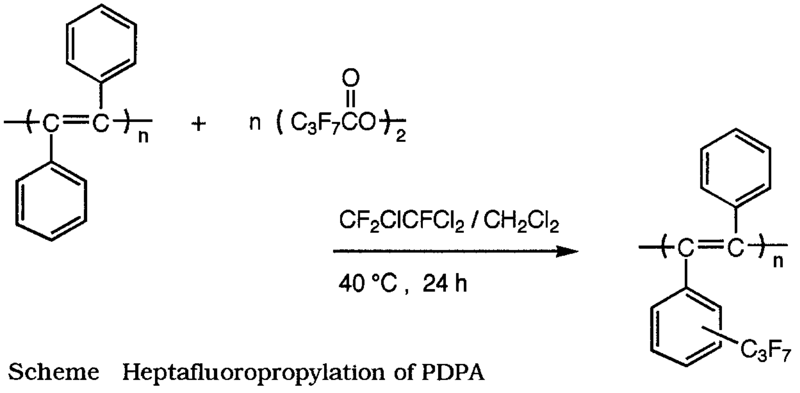
Bis(perfluoroalkanoyl) peroxides are useful reagents for the introduction of a perfluoroalkyl group to aromatic rings under mild conditions.[4] The physical behavior and potential applications of compounds fluorinated in this way have been studied.[5,6,7]

In the study reported here, polystyrene(PSt), poly(2,6-dimethyl-*p*-phenylene oxide)(PPO), and poly(diphenylacetylene)(PDPA) were perfluoroalkylated with bis(heptafluorobutyryl) peroxide, after which use of the modified polymers as separation membranes was evaluated.

Experimental

Materials

Bis(heptafluorobutyryl) peroxide was obtained from NOF Corporation as



Scheme Heptafluoropropylation of PDPA

a 5 wt% 1,1,2-trichlorotrifluoroethane(F113) solution. Tantalum pentachloride and tetrabutyltin were obtained commercially and used without further purification. Styrene and diphenylacetylene were distilled from calcium hydride. Toluene distilled from calcium hydride was used as the polymerization solvent for diphenylacetylene.

Prepolymers

PSt ($\overline{\mathrm{Mn}}$: 4.5 x10^5, $\overline{\mathrm{Mw}}$ / $\overline{\mathrm{Mn}}$: 2.0; determined by gel permeation chromatography) was prepared by bulk polymerization with 0.01 mol% 2,2'-azobis(isobutyronitrile) at 60°C for 90 h (56% yield).

PPO ($\overline{\mathrm{Mn}}$: 2.3 x10^4, $\overline{\mathrm{Mw}}$ / $\overline{\mathrm{Mn}}$: 2.5; determined by gel permeation chromatography) was obtained commercially and purified by reprecipitation from ethanol.

PDPA was prepared by the polymerization of diphenylacetylene with a transition metal catalyst: Tantalum pentachloride (0.40 g, 1.1 mmol) and tetrabutyltin (0.78 g, 2.2 mmol) were dissolved in toluene (110 ml) in an argon atmosphere, and the mixture was aged with stirring at 80°C for 30 min.[8] Diphenylacetylene (13.0 g, 0.073 mol) was added to this catalyst solution and polymerized at 80°C for 24 h. The solution became heterogeneous as polymerization proceeded. The polymer was precipitated by pouring the mixture into a large amount of methanol. The precipitate was washed several times with methanol then dried in a vacuum to a constant weight (9.97 g, 77% yield).

Calcd. for $C_{14}H_{10}$: C, 94.35%; H, 5.66%.

Found: C, 94.22%; H, 5.78%.

PSt and PPO were soluble in dichloromethane but insoluble in F113, which were the solvents used for perfluoroalkylation. PDPA was insoluble in all the organic solvents used and so was granulated prior to use.

Perfluoroalkylation

In a typical experiment, a 5 wt% F113 solution of bis(heptafluorobutyryl) peroxide (3.6 g, 8.4 mmol) was added to PDPA (0.50 g, 2.8 mmol monomer unit) dispersed in dichloromethane (75 ml) in an argon atmosphere. The mixture was stirred magnetically at 40°C for 24 h then poured into methanol. The precipitate was filtered out and dried under a vacuum, which gave the heptafluoropropylated polymer (0.83 g). Tetrahydrofuran was added to this polymer, and the soluble part was recovered from methanol. The tetrahydrofuran–soluble part (0.80 g) with a molecular weight of 8.0×10^4 ($\overline{Mn}$) and a polydispersity of 2.3 ($\overline{Mw} / \overline{Mn}$) was used for further characterization.

IR (cm^{-1}): 1350 (CF_3), 1230 (CF_2); found: C, 60.5%.

The number of heptafluoropropyl groups incorporated into the polymer was calculated from the carbon content.

Film Preparation

The films of the modified polymers were prepared by casting ca. 5 wt% solutions of PDPA in tetrahydrofuran, PSt and PPO in chloroform, on a glass surface. The solvents were evaporated at room temperature, and the films formed were dried under a vacuum at 40°C for 24 h.

Permeability Measurement

The gas permeabilities of the polymer films were estimated at 25°C by gas chromatography with air (O_2, N_2) and mixed gases (CO[10%], CH_4[27%], CO_2[7%], N_2[56%]), the upstream sides of the membranes being maintained at atmospheric pressure and 113 cmHg respectively, and the downstream sides at ca. 10^{-2} mmHg. The permeability coefficient P was determined from the slope of time–permeate volume curve in the steady state and the diffusion coefficient D was estimated by the time–lag method.[9] The apparent solubility coefficient S was calculated from the former two coefficients using equation: $S=P/D$, although the glass transition temperature of the polymer was higher than 25 °C.

In the pervaporation, aqueous ethanol was fed to the upper sides of the membranes, the downstream sides being maintained at ca. 10^{-1} mmHg. Under this condition, the membranes were allowed to stand overnight. Permeates were sampled after steady states had been reached. The composition and flux of the permeates were determined at 25°C with a gas chromatograph connected directly to the pervaporation cell. The permeation rate, P in $g{\cdot}m{\cdot}m^{-2}h^{-1}$, was calculated by correcting the flux for the membrane thickness. The separation factor, α, a measure of the preferential permeation of component A, was defined as the value obtained by dividing the concentration ratio Y_A/Y_B in the permeate by the concentration ratio X_A/X_B in the feed, A indicating ethanol and B water.

Instruments

IR spectra were obtained with a JASCO IR-810 infrared spectrophotometer. Molecular weights of the polymers were estimated with a Toso HLC-802A GPC with tetrahydrofuran as the eluent. Gas permeability coefficients of the polymer films were measured with a Yanako GTR-10. Pervaporation was done with a Yanako GTR-12L.

Results and discussion

Results of the perfluoroalkylation of PSt, PPO, and PDPA by bis(heptafluorobutyryl) peroxide are shown in Table 1. The reactions, except for PSt and PPO in the dichloromethane solutions, were heterogeneous, the polymers becoming partially soluble as the reactions proceeded.

Table 1 Heptafluoropropylation Results [a]

Feed						Polymer		
polymer	(g)	solvent	(ml)	peroxide [b] (g)	yield [c] (g)	C_3F_7 cont.[d]	$\overline{\mathrm{Mn}}$ [e] (10^4)	$\overline{\mathrm{Mw}}$ / $\overline{\mathrm{Mn}}$
PSt	1.0	CH_2Cl_2	80	6.1 (1.5eq.)	2.5 (2.5)	0.96	6.5	1.6
PSt	1.0	CH_2Cl_2	80	4.1 (1.0)	2.1 (2.1)	0.69	8.9	1.9
PSt	1.0	CH_2Cl_2	80	1.6 (0.40)	1.4 (1.4)	0.31	7.5	2.0
PSt	2.0	CH_2Cl_2	160	0.82 (0.10)	2.3 (2.3)	0.08	11	2.3
PSt	2.0	CH_2Cl_2	160	0.08 (0.01)	2.0 (2.0)	0.01	12	2.0
PSt	0.50	F113	40	3.1 (1.5)	1.4 (0)	1.20	-	-
PSt	1.0	F113	80	3.9 (0.95)	2.2 (0)	0.74	-	-
PDPA	0.50	CH_2Cl_2	75	3.6 (1.5)	0.83 (0.82)	0.46	8.0	2.3
PDPA	1.0	CH_2Cl_2	50	2.4 (0.5)	1.4 (0.92)	0.22	5.4	2.9
PDPA	1.0	CH_2Cl_2	25	1.2 (0.25)	1.2 (0.19)	0.19	4.0	2.7
PDPA	0.50	F113	50	2.4 (0.95)	0.97 (0)	0.57	-	-
PPO	1.0	CH_2Cl_2	35	1.8 (0.50)	1.2 (1.2)	0.36	1.6	1.8
PPO	1.0	F113	35	1.8 (0.50)	1.4 (0)	0.31	-	-

a Reactions were carried out at 40°C for 24h.

b Bis(heptafluorobutyryl) peroxide added as a 5 wt% F113 solution. The mole ratio of the peroxide to the benzene rings in the polymer is given in parentheses.

c Methanol-insoluble part. The yield of the tetrahydrofuran-soluble part is given in parentheses.

d Number of heptafluoropropyl groups per benzene ring calculated from the C content of the polymer for the tetrahydrofuran-soluble part.

e Estimated by GPC with tetrahydrofuran as the eluent and correlated to standard polystyrenes. Polymers with low molecular weights had been removed by reprecipitation.

All the polymers recovered by reprecipitation from methanol had increased weights, and the fluorine content of the polymers increased with the amount of peroxide used. For example, in the homogeneous reactions of PSt with the peroxide when dichloromethane was used, the heptafluoropropyl contents of the polymers could be controlled by the amount of peroxide added; *i.e.*, ca. 70% peroxide reacted with the polymer to give the heptafluoropropyl group.

The molecular weights of the recovered polymers were lower than those of the parent polymers when dichloromethane was the co-solvent; whereas, the reactions in F113 afforded insoluble polymers. In the presence of dichloromethane, main chain scission of the polymers may occur radically. As for PDPA, the absence of the carbonyl groups, which could have been formed by the reaction of the conjugated double bonds in its main chain with peroxide, was confirmed by the infrared spectra.[10]

Perfluoroalkylation with peroxides is described by a single electron transfer mechanism from the aromatic nucleus of the substrate to the peroxide.[4,10] As the reactivity of heptafluoropropylated benzene rings was low, because of the electron-withdrawing nature of the perfluoroalkyl group, each benzene ring first would be substituted by, at most, one heptafluoropropyl group.

The lowering of the molecular weight improved the solubility of the modified polymers, making it possible to prepare their films by the solution casting technique.

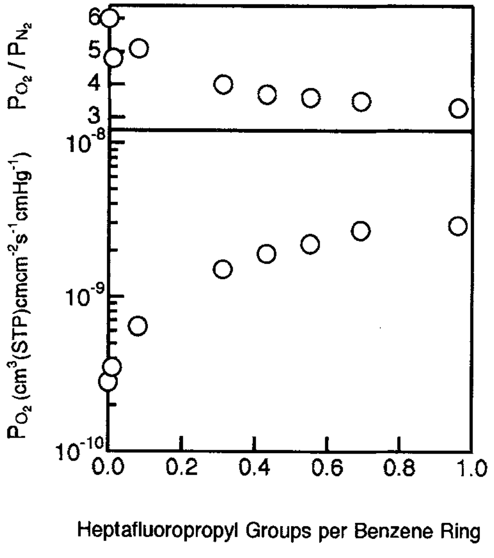


Figure 1 Oxygen Permeability and Selectivity in Heptafluoropropylated PSts

The usefulness of the prepared polymers as gas separation membranes was evaluated. Poly(phenylene oxide)s and substituted polyacetylenes are highly gas permeable, and chemically modified polystyrenes also have improved gas permeability.[11,12,13]

Figure 1 shows the oxygen permeabilities of PSts with various heptafluoropropyl contents. The perfluoroalkylated PSt had enhanced oxygen permeability which was related to the increase in the fluorine content of the polymer. The PSt, which had substitutions for 96% of its benzene rings, had tenfold the

Table 2 Gas Permeation Behavior of Heptafluoropropylated PSt [a]

Polymer	P_{O_2} [b]	P_{N_2} [b]	D_{O_2} [c]	D_{N_2} [c]	S_{O_2} [d]	S_{N_2} [d]
PSt	0.28	0.047	0.77	0.21	3.7	2.3
PSt–C_3F_7 (0.96) [e]	2.9	0.89	6.5	3.1	4.4	2.9

a Measured at 25°C.

b Permeability coefficient in $10^{-9}cm^3(STP)cm\ cm^{-2}sec^{-1}cmHg^{-1}$.

c Diffusion coefficient in $10^{-7}cm^2sec^{-1}$.

d Solubility coefficient in $10^{-3}cm^3(STP)cm^{-3}cmHg^{-1}$.

e Number of heptafluoropropyl groups per benzene ring in the polymer.

oxygen permeability coefficient of the original polymer; but, the permselectivity for O_2 to N_2 was a decreasing function of permeability. The permeability coefficients were divided into diffusion and apparent solubility coefficients, and the results are shown in Table 2. The diffusion coefficients for both oxygen and nitrogen were remarkably enhanced by the introduction of heptafluoropropyl groups into the polymer, while the solubility coefficients changed a little. Thus the large gas permeability of the heptafluoropropylated PSt is mainly brought about by the increased diffusion coefficient.

Table 3 gives the gas permeabilities of the modified PPO and PDPA. The PDPA, which had substitutions for 46% of its benzene rings, had the best gas permeability in these heptafluoropropylated polymers, about twice that for poly(dimethylsiloxane).[11]

Table 3 Gas Permeability Coefficients of Heptafluoropropylated Polymers [a]

Polymer	P ($10^{-9}cm^3(STP)cm\ cm^{-2}sec^{-1}cmHg^{-1}$)				
	N_2	O_2	CO	CH_4	CO_2
PPO	0.50	2.2	-	-	-
	(1.0) [b]	(4.4)			
PPO–C_3F_7(0.31) [c]	1.7	6.0	2.2	1.6	24
	(1.0)	(3.5)	(1.3)	(0.94)	(14)
PDPA–C_3F_7(0.22)	24	56	-	-	-
	(1.0)	(2.3)			
PDPA–C_3F_7(0.46)	46	92	56	46	330
	(1.0)	(2.0)	(1.2)	(1.0)	(7.2)

a Measured at 25°C.

b Relative value to P_{N_2}.

c Number of heptafluoropropyl groups per benzene ring in the polymer.

Table 4 Pervaporation of Aqueous Ethanol through Heptafluoropropylated Polymers [a]

Polymer	P_{H2O} [b] ($x10^{-4}$)	P_{EtOH} [b] ($x10^{-4}$)	α^{EtOH} [c]
PSt	0.99	0.0033	0.034
PSt–C_3F_7 (0.08)[d]	1.2	0.0079	0.070
PSt–C_3F_7 (0.96)	1.2	0.026	0.24
PDPA–C_3F_7 (0.46)	12	5.7	4.8

a $[EtOH]_{feed}$ = 8.8 wt%. Measured at 25°C.

b Permeation rate in $g \cdot m \cdot m^{-2} h^{-1}$.

c Defined as $\alpha = (Y_{EtOH} / Y_{H2O}) / (X_{EtOH} / X_{H2O})$, where X and Y are the respective weight fractions in the feed and permeate.

d Number of heptafluoropropyl groups per benzene ring in the polymer.

The main chain structure of the polymer remains an important factor in gas permeation through polymer films even when the polymers have been highly perfluoroalkylated.

In the pervaporation of aqueous alcohol, the hydrophobicity introduced by perfluoroalkyl groups to the polymers is thought to be favorable for alcohol to dissolve in the polymers. Results of pervaporation of an aqueous ethanol solution in PSt and PDPA are shown in Table 4.

The permeation rate of ethanol became high in heptafluoropropylated PSt and resulted in a large α value, and the permeation rate of water was almost identical with that of the parent PSt. The polymer, however, retained water permselectivity of PSt even when perfluoroalkylated.

Pervaporation is also controlled by the mass transport mechanism described in the solution–diffusion model.[14] Therefore the solubility of ethanol in PSt could not be so enhanced by perfluoroalkylation as to overcome the disadvantageous diffusivity of ethanol caused by its molecular dimensions.[15]

Unlike the PSts, heptafluoropropylated PDPA is highly liquid permeable and ethanol permselective. PDPA, which has a rigid main chain consisting of alternating double bonds, must have voids between its polymer molecules, and these are considered to reduce the barrier in ethanol diffusion. The disadvantageous diffusivity of ethanol therefore is not significant in this polymer.

In conclusion, polymers perfluoroalkylated with bis(heptafluorobutyryl) peroxide have high gas and vapor permeability. Their permeabilities depend on those of the parent polymers even when they have been highly perfluoroalkylated.

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