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Trifluoromethylation by bis(trifluoroacetyl) peroxide of polymers bearing benzene rings

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Abstract

Bis(trifluoroacetyl) peroxide was prepared in good yield by the reaction between trifluoroacetic anhydride and sodium peroxide under anhydrous conditions. Polymers bearing benzene rings, polystyrene, poly(phenylene oxide) and poly(diphenylacetylene) were modified chemically by the peroxide. The resulting trifluoromethylated polymers have good solubilities in common organic solvents, and their cast films have good water repellency. The trifluoromethylated poly(diphenylacetylene)s have high gas and vapor permeabilities. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Fluoropolymers; Trifluoromethyl; Peroxide

1. Introduction

Perfluoroalkanoyl peroxides have marked decomposition abilities as compared with nonfluorinated analogs [1–7]. This enhanced decomposition is related to the stability of the perfluoroalkyl radical which leads to homolytic concerted O–O cleavage and decarboxylation. Perfluoroalkanoyl peroxides therefore are good sources of perfluoroalkyl radicals and useful radical initiators in the polymerization of fluoroolefines, acrylates, methacrylates, vinylsilanes, etc [8–11].

On the other hand, perfluoroalkanoyl peroxides react with such electron-rich olefins as styrene, vinylether and allylsilanes affording adducts via electron transfer rather than polymers [12–14]. Molecular orbital calculation showed that these peroxides have very low energy levels for the antibonding O–O bonds as compared with nonfluorinated molecules, indicative that the peroxides are good electron acceptors [15]. In fact they are effective electron acceptors, even from such relatively poor electron-donor aromatics as benzene and chlorobenzene [16,17].

Perfluoroalkanoyl peroxides also react with benzene rings in polymers, producing perfluoroalkylated polymers via electron transfer. This makes them useful as reagents with which to modify polymers with perfluoroalkyl groups [18–24]. Such a modification method must facilitate the development of novel fluorinated polymers, otherwise troublesome monomer synthesis and polymerization processes would be required.

Bis(trifluoroacetyl) peroxide, prepared by the reaction between trifluoroacetic anhydride and sodium peroxide in anhydrous acetonitrile, was used to trifluoromethylate various polymers (Fig. 1). Of the perfluoroalkanoyl peroxides, bis(trifluoroacetyl) peroxide is fairly stable but less accessible because of the difficulty in preparation, the peroxide being easily hydrolyzed in aqueous media [25,26].

Because of the low aggregation energies of fluorinated substances, trifluoromethyl groups introduced into polymers are expected to enhance polymer solubility in common organic solvents, thereby improving the processability of the polymers. Properties of the modified polymers, water repellency and gas and vapor permeabilities, which also are markedly affected by fluorinated groups, are evaluated.

2. Experimental

2.1. Materials

Granular sodium peroxide (small beads, 95%) purchased from Fluka was used without further purification. Trifluoroacetic anhydride obtained commercially was purified by distillation. Acetonitrile was distilled from phosphorous pentaoxide prior to its use.

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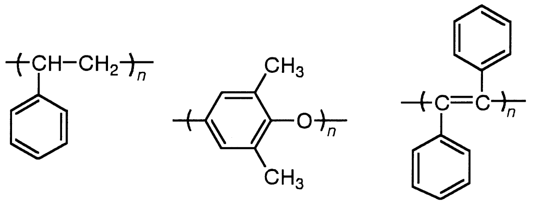


PSt **PPO** **PDPA**

Fig. 1. Prepolymers.

2.2. Bis(trifluoroacetyl) peroxide

Bis(trifluoroacetyl) peroxide was prepared as follows: sodium peroxide (3.90 g, 50.0 mmol) was dispersed in anhydrous acetonitrile (20 ml) by vigorous mechanical stirring at 0°C under an argon atmosphere. Trifluoroacetic anhydride (21.0 g, 100 mmol) was added dropwise to the dispersion over 30 min. As inductive delay of the reaction may occur, special caution must be taken during the initial stage of the addition to avoid an explosion. The reaction proceeded smoothly, as confirmed by the turbidity and foaming of the reaction mixture, fine white precipitates of sodium trifluoroacetate being formed while pale yellow granules of sodium peroxide were consumed. After additional stirring for 10 min at 0°C, volatiles were evaporated under vacuum and collected in a cold trap (−78°C) to give the peroxide solution (21.9 g). This solution was characterized by IR and ^{19}F NMR, which showed that bis(trifluoroacetyl) peroxide was the sole volatile product collected and that only a trace of trifluoroacetic anhydride remained. The amount of bis(trifluoroacetyl) peroxide (9.04 g, 80.0% yield) in the solution was determined by iodometry. The highly concentrated peroxide solution can decompose with explosive violence, therefore it is safely handled only at a relatively low temperature; shock and contact with metals must be avoided.

Bis(trifluoroacetyl) peroxide: ^{19}F NMR (CD_3CN): −70.58 ppm, IR (CH_3CN): 1682 cm^{-1}.

Conveniently, the peroxide to be used in the trifluoromethylation reaction could be prepared by dilution of the reaction mixture with pre-cooled 1,1,2-trichlorotrifluoroethane (80 ml) immediately after the addition of trifluoroacetic anhydride to the sodium peroxide suspension and additional stirring. This mixture was filtered to remove any unreacted sodium peroxide, sodium trifluoroacetate, or uncharacterized by-products. The amount of bis(trifluoroacetyl) peroxide (9.17 g, 81.1% yield) in the filtrate (130 g, 7.05 wt%) was determined by iodometry, after which the peroxide solution was diluted to 5.0 wt% with 1,1,2-trichlorotrifluoroethane and acetonitrile (4/1 by vol.) and then refrigerated.

The decomposition rates of the peroxide were measured as follows: peroxide solutions of 5.0 wt% were placed in glass ampoules and degassed by successive freeze–thaw cycles. The ampoules were sealed, and the peroxide allowed to decompose in vacuo at a regulated temperature. After appropriate periods, the residual amounts of peroxide were determined by iodometry. The apparent first-order rate constants of peroxide decomposition and half-lives were obtained from the slopes of semilogarithmic plots of the peroxide concentration against time.

2.3. Trifluoromethylation of benzene

Benzene was added to a 5.0 wt% solution of bis(trifluoroacetyl) peroxide in 1,1,2-trichlorotrifluoroethane and acetonitrile (4/1 by vol.). The mixture was stirred magnetically at 40°C for 24 h under an argon atmosphere. The compositions of the products were determined by gas chromatography.

2.4. Prepolymers

Polystyrene (PSt; $\bar{M}_n$ 5.00×10^4, $\bar{M}_w/\bar{M}_n$ 1.06), a monodispersed standard PSt, was purchased from Pressure Chemical Company.

Poly(2,6-dimethyl-*p*-phenylene oxide) was obtained commercially and purified twice by reprecipitation from a mixture of chloroform and ether (3/5 by vol.) (PPO; $\bar{M}_n$ 5.35×10^4, $\bar{M}_w/\bar{M}_n$ 1.42).

Poly(diphenylacetylene) (PDPA) was prepared by polymerization of diphenylacetylene with tantalum pentachloride and tetrabutyltin as the catalysts [22]. As PDPA was insoluble in all the organic solvents used, it was granulated into fine powder prior to use.

2.5. Trifluoromethylation of polymers

In a typical experiment, bis(trifluoroacetyl) peroxide (1.27 g, 5.61 mmol) as a 5.0 wt% solution in 1,1,2-trichlorotrifluoroethane and acetonitrile (4/1 by vol.), was added to PDPA (0.250 g, 1.40 mmol monomer unit) dispersed in 1,1,2-trichlorotrifluoroethane (4 ml) under an argon atmosphere. The mixture was stirred magnetically at 40°C for 24 h then evaporated under vacuum. Tetrahydrofuran was added to the residue, and the resulting mixture poured into water. The precipitated polymer was filtered out and dried under vacuum then further purified by reprecipitation to give the trifluoromethylated polymer (0.460 g).

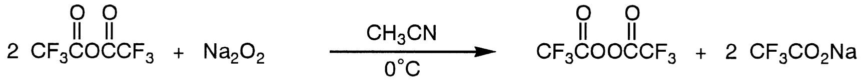
^{19}F NMR ($(CD_3)_2CO$): −57.89, −61.37 and −73.44 ppm; found: C, 56.60%.

2.6. Film preparation

Trifluoromethylated polymer films were prepared by casting ca. 5 wt% tetrahydrofuran solutions of PDPA, PSt or PPO on a poly(tetrafluoroethylene) surface. The solvent was evaporated at room temperature, and the film formed peeled off and dried at 40°C for 24 h under vacuum.

2.7. Gas and vapor permeability measurements

Gas permeabilities of the polymer films were estimated at 25°C with air (O_2, N_2). After evacuation of both sides of the



$$2\ CF_3\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CF_3 + Na_2O_2 \xrightarrow[0^\circ C]{CH_3CN} CF_3\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}CF_3 + 2\ CF_3CO_2Na$$

Scheme 1.

film to ca. 10^{-2} Torr, the upstream side was filled with the air. The amounts of permeating gases on the downstream side were measured by gas chromatography. The permeability coefficient was determined from the slope of the time-course permeate volume curve in the steady state.

A 10 wt% aqueous ethanol was fed at 25°C to the upper side of the film in a pervaporation cell, the downstream side being maintained at ca. 10^{-1} Torr, and the film allowed to stand overnight. The permeates were collected in a cold trap. The total flux was determined by weighing the permeate mixture after an appropriate period. The composition of the mixture was determined by gas chromatography. The flux of each component was calculated from the total flux and the composition and converted to the permeation rate, P, in g m m^{-2} h^{-1}, by correction for the area and thickness of the film.

2.8. Instruments

Infrared spectra were obtained with a Shimadzu FTIR-8600PC spectrophotometer. ^{19}F NMR (282.2 MHz) was measured with a Varian UNITY INOVA-300 device, and the chemical shifts defined as δ values relative to $CFCl_3$. Molecular weights of the polymers were correlated to those of standard PSts using a TOSO HLC-802A gel permeation chromatograph with TOSOH GMH6 columns and tetrahydrofuran as the eluent. Contact angles of water droplets to the polymer film surface were measured with an Erma G-1 goniometer. Gas permeability coefficients of the polymer films were measured with a Yanako GTR-10.

3. Results and discussion

Bis(trifluoroacetyl) peroxide is useful both as an initiator in radical polymerization of fluoroolefines and as a reagent to introduce trifluoromethyl groups into aromatic molecules. Thermally, it is fairly stable and easy to handle, whereas bis(heptafluorobutyryl) peroxide and bis(pentadecafluorooctanoyl) peroxide decompose smoothly even at room temperature.

Of the perfluoroalkanoyl peroxides, bis(trifluoroacetyl) peroxide has had fewer applications because of its poor accessibility. It has been prepared by the addition of trifluoroacetic anhydride to sodium peroxide or hydrogen peroxide in a two-phase mixture of water and 1,1,2-trichlorotrifluoroethane or ether [7,8,27]. Yields have been limited because of its easy hydrolyzability [25,26], whereas other bis(perfluoroalkanoyl) peroxides that have long, strongly hydrophobic perfluoroalkyl groups have been similarly prepared, most in yields above 80% [28,29].

$$(CF_3CO_2)_2 \longrightarrow CF_3{-}CF_3 + 2\ CO_2$$

Scheme 2.

To improve the yield of the bis(trifluoroacetyl) peroxide preparation, the reaction was done under anhydrous conditions [30] (Scheme 1). Fine granular sodium peroxide dispersed in anhydrous acetonitrile reacted smoothly with trifluoroacetic anhydride at 0°C, giving the peroxide in 80% yield. Conveniently, the reaction mixture could immediately be diluted with 1,1,2-trichlorotrifluoroethane and filtered to remove any unreacted sodium peroxide, sodium trifluoroacetate or uncharacterized by-products. An undiluted reaction mixture was evaporated and characterized by IR and ^{19}F NMR, showing that bis(trifluoroacetyl) peroxide was the sole volatile product collected and that only a trace of trifluoroacetic anhydride remained.

The spontaneous decomposition behavior of the peroxide in acetonitrile and in a 1,1,2-trichlorotrifluoroethane and acetonitrile mixture (4/1 by vol.) was evaluated by measuring the rate constants of decomposition (Scheme 2, Homolytic decomposition of bis(trifluoroacetyl) peroxide). Semilogarithmic time-course peroxide concentrations at appropriate temperatures were plotted, the slopes of the straight lines giving the apparent first-order decomposition rates of the peroxide (k_d). As Table 1 shows, the decomposition rate in acetonitrile is twice that in the 1,1,2-trichlorotri-fluoroethane and acetonitrile mixture, and the rate for the latter mixture is larger than that in 1,1,2-trichlorotrifluoroethane [7]. The acceleration presumably is due to the higher dielectric strength of the solvent.

With benzene as the electron-donor, decomposition of the peroxide is markedly accelerated as a result of electron transfer (Scheme 3, Trifluoromethylation of benzene via the electron transfer process). In the trifluoromethylation reactions with bis(trifluoroacetyl) peroxide, the peroxide undergoes more rapid decay than it does spontaneously [5–7,16,17].

Trifluoromethylation of benzene with the peroxide was done at 40°C. Results are shown in Table 2. With an equivalent amount of benzene, 95% of the peroxide had disappeared after 24 h at 40°C; about 60% of the peroxide reacted with benzene to give the trifluoromethyl group, the remaining 35% having decomposed spontaneously without giving the trifluoromethyl group to benzene. The major product was trifluoromethylbenzene, with disubstituted benzenes as minor products, because, once benzene is trifluoromethylated, its ability to donate electrons becomes poor, and formation of the disubstituted benzene would be restricted. When there was excess peroxide, a large amount remained after 24 h at 40°C, and the yields of trifluoromethylbenzene and the disubstituted benzenes increased.

Table 1
Rate constants for the spontaneous decomposition and half-lives of bis(trifluoroacetyl) peroxide (peroxide in a 5 wt% solution; in vacuo)

k_d (10^{-5} s^{-1})	$t_{1/2}$ (h)	Solvent	Temperature (°C)
1.19	16.2	acetonitrile	40
0.734	26.2	mixed[a]	40
6.34	3.04	acetonitrile	50
3.50	5.50	mixed[a]	50
3.08[b]	6.25	CCl_2FCClF_2	50

[a] CCl_2FCClF_2/acetonitrile (4/1 by volume).

[b] Data from Ref. [7].

Bis(trifluoroacetyl) peroxide was allowed to react with the polymers PSt, PPO and PDPA, giving trifluoromethyl groups to their benzene rings (Scheme 4 and Table 3). The prepolymers were dispersed in small amounts of 1,1,2-trichlorotrifluoroethane, and the peroxide solutions added to the dispersions. As the reactions proceeded, the polymers became partly soluble in the reaction solvents. By the incorporation of trifluoromethyl groups, all the polymers, recovered by reprecipitation from water, increased in weight. The trifluoromethyl content of each polymer increased with the amount of peroxide used.

Gel permeation chromatograms for the PSts are shown in Fig. 2. The elution peak of the PSt prepolymer has shifted to the high molecular weight region after the reaction. The peak of the each recovered polymer has a discernible shoulder on the high molecular weight side and a tailing. The tailing is pronounced for **PSt2**, which corresponds to the polymer's low molecular weight and large polydispersity (Table 2).

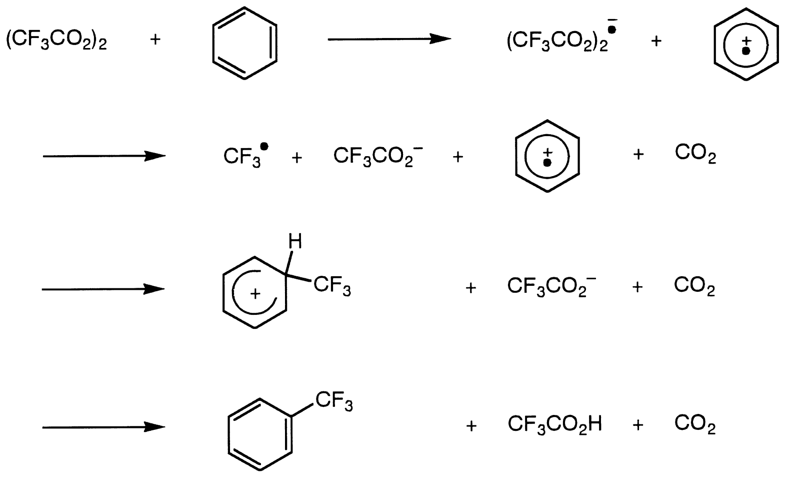
Because the trifluoromethylation reaction proceeds via single electron transfer from the substrate to the peroxide, the trifluoromethyl radical formed must exist in close proximity to the radical cation of the substrate, as a radical pair in a solvent cage, such that subsequent coupling between the radical and radical cation would take place preferentially [16], but once the substrate is trifluoromethylated it would become a poor electron-donor. With excess peroxide in the feed, inevitable homolytic cleavage of the peroxide therefore becomes pronounced, producing free trifluoromethyl radicals which, in the reaction with polymers, leads to unfavorable cross-linking and main-chain scission of the polymer molecules.

In the series of the PPO reactions, the recovered polymers had decreased molecular weights and increased polydispersities as the mole ratio of the peroxide to the benzene rings in the polymer increased in the feed. The control experiment confirmed that trifluoroacetic acid, which forms in the trifluoromethylation reaction, did not affect the molecular weight of the parent PPO. The decrease in the molecular weight of PPO in the trifluoromethylation reaction therefore is thought to be caused by radicals.

As for the PDPAs, a multimodal curve was observed in the GPC when the mole ratio of peroxide to the benzene rings in the polymer was small in the feed. This might be because the parent PDPA was insoluble in the reaction solvent, and heterogeneity remained in the mixture throughout the reaction. The trifluoromethylated PDPAs had unimodal molecular weight distributions when a large amount of peroxide was used.

Whereas the parent PDPA is not soluble in common organic solvents, the trifluoromethylated PDPA (**PDPA2**) is completely soluble in acetone, ethyl acetate, ether, tetrahydrofuran and dimethylformamide; slightly soluble in acetonitrile, methanol, dichloromethane and hexafluorobenzene; but insoluble in hexane, toluene and 1,1,2-trichlorotrifluoroethane. Trifluoromethylated PSt and PPO retain the good solubilities of their parent polymers.

The trifluoromethyl group is a component which can give extremely low surface energy to a material's surface [31]. Trifluoromethylated polymers therefore would have good water and oil repellency. Polymer water repellencies were estimated by measuring the contact angles of water droplets on the polymer film surfaces. Results are shown in Table 3.



Scheme 3.

Table 2
Trifluoromethylation of benzene with bis(trifluoroacetyl) peroxide (peroxide in 1,1,2-trichlorotrifluoroethane and acetonitrile (4/1 by volume))

Peroxide/benzene[a]	Peroxide residue (%)[b]	Benzenes (%)[c]			
		H	CF_3	*p*-$(CF_3)_2$	*m*-$(CF_3)_2$
1.0	4.9	41.8	56.6	0.6	1.0
2.0	15.2	11.8	80.6	2.8	4.8

[a] Mole ratio in feed.

[b] After 24 h at 40°C.

[c] Determined by gas chromatography; no *ortho*-disubstituted was found.

Table 3
Trifluoromethylation of polymers with benzene rings

Polymer	Feed		Yield (g)	$\bar{M}_n$ (10^4)[a]	$\bar{M}_w/\bar{M}_n$[a]	θ (°)[b]
	Prepolymer (g)	Peroxide (g)[c]				
PSt				5.00	1.06	90.9
PSt0.5	PSt, 0.250	0.271 (0.5)	0.286 (0.16)[d]	5.53	1.08	94.0
PSt1	PSt, 0.250	0.543 (1.0)	0.319 (0.65)	9.36	1.62	96.7
PSt2	PSt, 0.250	1.08 (2.0)	0.428 (0.80)	4.16	2.41	98.3
PPO				5.35	1.42	85.9
PPO0.5	PPO, 0.500	0.470 (0.5)	0.616 (0.34)	3.29	1.88	99.0
PPO1	PPO, 0.250	0.470 (1.0)	0.332 (0.73)	2.77	2.14	99.2
PPO2	PPO, 0.250	0.941 (2.0)	0.415 (0.77)	1.43	2.19	101.5
PDPA				insol.	–	–
PDPA0.5	PDPA, 0.250	0.317 (0.5)	0.309 (0.23)	6.09	9.29[e]	93.2
PDPA1	PDPA, 0.250	0.634 (1.0)	0.364 (0.69)	6.68	1.76	92.8
PDPA2	PDPA, 0.250	1.27 (2.0)	0.460 (1.01)	6.47	1.90	97.1

[a] Molecular weight determined by GPC (eluent: tetrahydrofuran).

[b] Contact angle of water droplet.

[c] Bis(trifluoroacetyl) peroxide added as a 5 wt% solution; the mole ratio of the peroxide to the benzene rings in the polymer is given in parentheses.

[d] Number of CF_3 groups per benzene ring in the polymer in parentheses. Estimated by ^{19}F NMR with C_6F_6 as the internal standard.

[e] Multimodal.

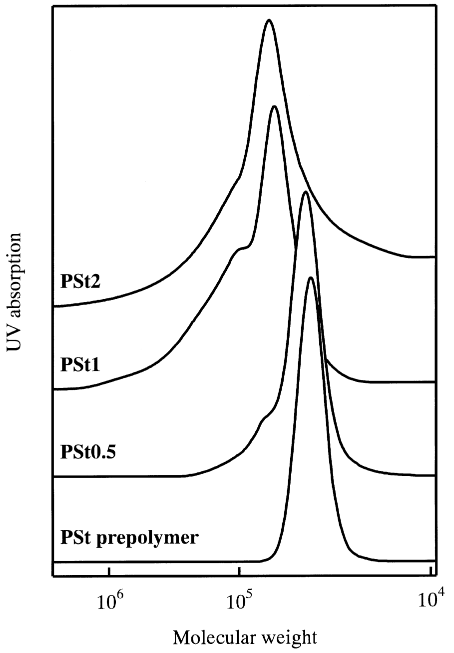


Fig. 2. Gel permeation chromatograms of trifluoromethylated PSts.

All the modified polymers have good water repellency, depending on the amount of the incorporated trifluoromethyl groups.

Although highly fluorinated crystalline polymers, such as poly(tetrafluoroethylene), have very poor gas permeability owing to their high crystallinity [32], polymers with fluoro-substituents are expected to have high gas permeability as well as high chemical and thermal stability. This is because highly fluorinated liquids have high gas solubility [33,34]. Several classes of fluorinated polymers have been

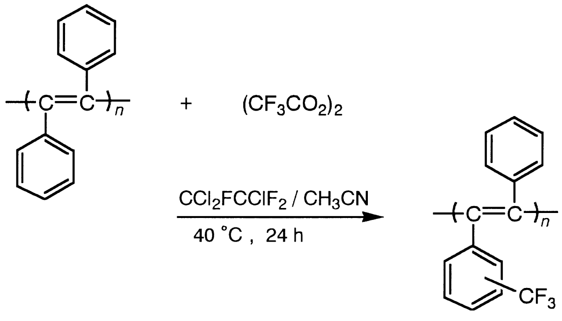
Table 4
Gas and vapor permeabilities of trifluoromethylated poly(diphenylacetylene)s (at 25°C)

Polymer	P_{O_2}[a]	P_{N_2}[a]	P_{O_2}/P_{N_2}	P_{EtOH}[b]	P_{H_2O}[b]	α[c]
PDPA1	6.59	3.25	2.03	1.68	3.39	4.46
PDPA2	7.42	3.78	1.96	2.29	3.71	5.56

[a] Gas permeability coefficient in 10^{-8} cm^3(STP) cm cm^{-2} s^{-1} $cmHg^{-1}$.

[b] Vapor permeation rate in 10^{-3} g m m^{-2} h^{-1}.

[c] Defined as $\alpha = (Y_{EtOH}/Y_{H_2O})/(X_{EtOH}/X_{H_2O})$, where X and Y are the respective weight fractions in the feed and permeate.



Scheme 4.

synthesized, and their potential usefulness for gas separation has been demonstrated [22,35–38].

The main-chain structure of the polymer as well as the substituents has an important function in gas permeability. Rubbery poly(dimethylsiloxane) has marked gas permeability due to the high mobility of its chains [32], whereas glassy poly(1-trimethylsilylpropyne), a substituted polyacetylene, has the highest gas permeability of the known polymers, its oxygen permeability coefficient being about ten times that of poly(dimethylsiloxane) [39]. A rigid backbone and large substituents would give the polymer a large free volume, allowing easy passage of penetrating gases.

Gas and vapor permeabilities of the trifluoromethylated PDPAs were evaluated for air and aqueous alcohol. The polymers have good gas permeability (Table 4), the oxygen permeability coefficients being of the same magnitude as the coefficient of poly(dimethylsiloxane). This high gas permeability is attributed to the polymer structure which consists of a rigid backbone and bulky fluorinated substituents [40]. The more trifluoromethylated PDPA has a higher gas permeability, but its permselectivity (P_{O_2}/P_{N_2}) is slightly decreased.

In the pervaporation of aqueous alcohol, the polymers had ethanol permselectivity of relatively high flux. Pervaporation is controlled by the mass transport mechanism described in the solution-diffusion model [41]. The hydrophobicity introduced by the trifluoromethyl groups is considered favorable for ethanol to dissolve in the polymers. Moreover, the presence of trifluoromethyl groups would expand the gaps between the polymer molecules that are considered to reduce the barrier in ethanol diffusion [42].

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