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Synthesis of galvinoxyl unit-containing derivatives of poly(phenylacetylene) and polystyrene, and oxygen permeation behavior of their membranes

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Abstract

Poly(phenylacetylene) and polystyrene which contain galvinoxyl and trimethylsilyl units were synthesized by copolymerization of the corresponding monomers or polymer reaction of the corresponding methyl benzoate polymers with [3,5-di-*tert*-butyl-4-(trimethylsiloxy)-phenyl]lithium. The copolymers obtained from (4-trimethylsilyl)phenylacetylene and (4-ethynylphenyl)hydrogalvinoxyl using [Rh(norbornadiene)Cl]$_2$ catalyst had very high molecular weights. On the contrary, the copolymers of (4-trimethylsilyl)styrene and methyl 4-vinylbenzoate nearly completely reacted with [3,5-di-*tert*-butyl-4-(trimethylsiloxy)phenyl]lithium to give the corresponding galvinoxyl-copolymers with high molecular weights. The hydrogalvinoxyl polymers were converted to the corresponding polyradicals by chemical oxidation. These copolymers and polyradicals could be fabricated to self-supporting membranes. We succeeded in obtaining such stable polyradical membranes that the initial spin concentration was maintained for a few days. The oxygen permselectivity ($\alpha = P_{O_2}/P_{N_2}$) increased and the oxygen permeability (P_{O_2}) decreased as galvinoxyl units increased, owing to the rigid character of galvinoxyl moiety.

Keywords: Polyradical; Polymeric solid membrane; Gas permeation

1. Introduction

Organic radicals are usually known as unstable transient intermediates in organic reactions. However, some of organic radicals such as radical crystals of galvinoxyl [1] and steric hindered nitroxyl [2] are so stable as to remain from a few months to a few years in ambient atmosphere. Polymers bearing a number of free radical groups, so-called polyradicals, were used for polymer antioxidants, redox resin and spin labeling [3]. Further, they have recently been regarded as building blocks to construct a molecule-based ferromagnet [4]. Polyradicals which have enough molding and thin-film forming ability, however, are not known because it is difficult to synthesize and stabilize them. On the contrary, we have found that polymers containing trimethylsilyl groups have good flexibility; i.e. poly(phenylacetylene) and poly(styrene) bearing trimethylsilyl groups, in particular, yielded tough membranes by casting the polymer solution, and their membranes displayed good oxygen permselectivity [5,6]. In this study, in order to obtain a new polyradical having good membrane forming ability, we synthesized copolymers of (4-ethynylphenyl)hydrogalvinoxyl (EPHG) with (4-trimethylsilyl)-phenylacetylene (TMSPA), and copolymers of (4-vinylphenyl)hydrogalvinoxyl (VPHG) with (4-trimethylsilyl)styrene (TMSSt), and oxidized the copolymers to yield the corresponding polyradicals, poly[(4-ethynylphenyl)galvinoxyl-*co*-(4-trimethylsilyl)phenylacetylene] (poly(EPG-TMSPA)) and poly[(4-vinylphenyl)galvinoxyl-*co*-(4-trimethylsilyl)styrene] (poly(VPG-TMSSt)), respectively. We also evaluated the oxygen permeability for the resulting copolymer membranes (see Scheme 1).

2. Experimental

2.1. Materials

EPHG [7], TMSPA [5], VPHG [8], (4-vinylphenyl)acetylgalvinoxyl (VPAcG) [8], TMSSt [6], methyl 4-vinylbenzoate (MVB) [8] and (2,6-di-*tert*-butyl-4-bromo- phenoxy)trimethylsilane [9] were synthesized as previously described. Methyl methacrylate (MMA) (Junsei Chemical) and octyl methacrylate (OMA) (Tokyo Chemical) were distilled

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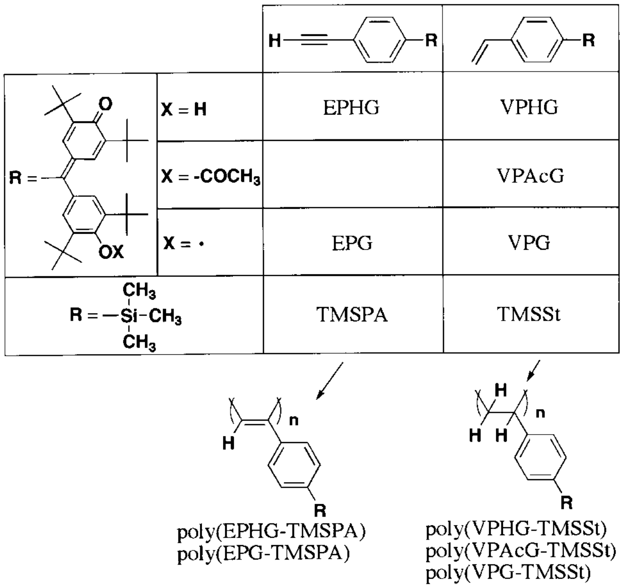

Scheme 1.

before use. 2,2′-Azobis(isobutyronitrile) (AIBN) (Tokyo Chemical) was purified by recrystallization from methanol. (Bicyclo[2.2.1]hepta-2,5-diene)chlororhodium(I) dimer catalyst ([Rh(C_7H_8)Cl]$_2$) (Aldrich) and *n*-butyllithium (Kanto Chemical, 1.6 M in hexane) were used without further purification. Other conventional reagents were used as received or purified by conventional method.

2.2. Polymerization

Polymerization catalyzed by [Rh(C_7H_8)Cl]$_2$ was carried out as follows. An appropriate amount of monomer (typically, 0.5–1.0 g) was placed in an Schlenk tube equipped with a three-way stopcock, a rubber septum and a Teflon-coated magnetic stirring bar. The tube was placed under vacuum, followed by a nitrogen backflush. Freshly distilled chloroform was transferred to the tube, and the monomers were dissolved with stirring. The determined amount of [Rh(C_7H_8)Cl]$_2$ and triethylamine dissolved in chloroform was added to the stirred monomers solution. The detailed polymerization conditions are tabulated in Table 1. The reaction solution was poured into hexane or methanol to yield polymer precipitate. The precipitate was washed with the precipitant and then dried in vacuo to give a yellow polymer.

Polymerization initiated by AIBN was carried out as follows. The aforementioned tube was charged with vinyl monomers and AIBN. The content of the tube was degassed and placed under nitrogen. Freshly distilled tetrahydrofuran (THF) was transferred to the tube when needed. The monomers mixture was stirred with heating the tube at 70–80°C. The detailed polymerization conditions are tabulated in Tables 2–4. After cooling, the reaction mixture was diluted and dissolved in THF, and was poured into hexane or methanol to precipitate the polymer. The precipitate was washed with the precipitant and then dried in vacuo to give a yellow polymer.

2.3. Formation of hydrogalvinoxyl moiety from carboxylate in the polymers

To the suspension of (2,6-di-*tert*-butyl-4-bromophenoxy)trimethylsilane in THF cooled to −70°C under nitrogen was slowly added 1.2 times amount of 1.6 M *n*-butyllithium in hexane. After the reaction between the two reagents proceeded to give a clear solution, the solution was stirred for about 15 min. Then *N*,*N*,*N*′,*N*′-tetramethylethylenediamine and the given amount of carboxylate polymer in THF were added in that order, and the solution was stirred for 2 h at −70°C accompanying the color change from clear to orange. The solution was warmed to room temperature and was stirred for 4 h. The resulting reddish brown solution was reacted with excess KOH aqueous solution overnight to form a dark bluish solution. Saturated NH_4Cl solution was added, and the organic layer was washed with water. After drying over anhydrous Na_2SO_4, the solution was concentrated and poured into hexane or methanol to yield polymer precipitate. The precipitate was washed with the precipitant and then dried in vacuo to give a yellow polymer.

Table 1
Copolymerization of EPHG with TMSPA in chloroform ($[\mathrm{EPHG}]_0 + [\mathrm{TMSPA}]_0 = [\mathrm{M}]_0 = 0.1$ mol/l, $[\mathrm{M}]_0/[[\mathrm{Rh}(C_7H_8)\mathrm{Cl}]_2]_0 = 100$, $[\mathrm{triethylamine}]_0/[[\mathrm{Rh}(C_7H_8)\mathrm{Cl}]_2]_0 = 20$, $CHCl_3$, 25°C, 0.5 h) and membrane preparation

Run	EPHG in feed (mol%)	Yield (%)	$\bar{M}_n$ ($\times 10^4$)[a]	$\bar{M}_w/\bar{M}_n$[a]	EPHG in polymer (mol%)[b]	Membrane forming ability[c]	Precipitant
1[d]	100	20	2.4	2.0	100	−	Hexane
2	70	33	9.7	2.5	58	+	Hexane
3	50	43	9.4	2.2	46	+	Hexane
4	30	71	16	3.0	22	++	Methanol
5	10	96	18	3.6	10	++	Methanol

[a] Determined from GPC calibrated by polystyrene standard.

[b] Determined from ^1H NMR.

[c] ++, Tough; +, brittle; −, poor.

[c] $[\mathrm{M}]_0 = 0.05$ mol/l, $[\mathrm{M}]_0/[[\mathrm{Rh}(C_7H_8)\mathrm{Cl}]_2]_0 = 50$.

Table 2
Copolymerization of VPHG and VPAcG with TMSSt (80°C, 3 h) or OMA (70°C, 12 h) in THF ($[M_1]_0 + [M_2]_0 = 1$ mol/l, THF)

M_1	M_2	M_2 in feed (mol%)	$[AIBN]_0/[M_2]_0$ (mol%)	Yield (%)	$\bar{M}_n$ ($\times 10^4$)[a]	$\bar{M}_w/\bar{M}_n$[a]	M_2 in polymer (mol%)[b]
TMSSt	VPHG	7.7	120	24	5.0	1.1	14
		7.7	38	0			
	VPAcG	7.2	41	22	3.1	1.4	36
OMA	VPHG	8.7	48	50	5.3	1.3	7.6
		8.7	14	0			
	VPAcG	8.1	16	68	6.0	1.1	9.0

[a] Determined from GPC calibrated by polystyrene standard.
[b] Determined from ^{1}H NMR.

2.4. Oxidation of hydrogalvinoxyl residue

Polyradical was prepared by chemical oxidation of hydrogalvinoxyl residue with PbO_2 or $K_3Fe(CN)_6$ under nitrogen in a glovebox as follows. Oxidation using PbO_2: a degassed benzene solution of hydrogalvinoxyl polymer (5 mM per galvinoxyl unit) was treated with 10 eq. of PbO_2, and was vigorously stirred for 0.5–2 h. After filtration the benzene solution was used for ESR measurement and membrane preparation. Oxidation using $K_3Fe(CN)_6$: a degassed benzene or chloroform solution of hydrogalvinoxyl polymer (5–10 mM per galvinoxyl unit) was treated with an alkaline solution (1 N NaOH aq) containing 10 eq. of $K_3Fe(CN)_6$. After vigorously stirring for 0.5 h, the organic layer was washed with water thoroughly, and dried over anhydrous Na_2SO_4. After filtration the benzene solution was used for ESR measurement and membrane preparation.

2.5. Membrane preparation

A 5 wt% (w/v) solution of a polymer in chloroform was cast on a Teflon sheet, and the solvent was evaporated for 12 h at room temperature. The resulting solid membrane was detached from the sheet and dried in vacuo for 24 h. Thickness (L) of the membranes was 80–110 μm.

Aforementioned polyradical solution was concentrated to ca 5 wt% (w/v) in vacuo, and was cast on a Teflon sheet under nitrogen in a glovebox. The solvent was evaporated under reduced pressure (15 cmHg) for 12 h at room temperature. The resulting solid membrane was detached from the sheet and dried in vacuo for 4 h. Thickness (L) of the membranes was 70 μm.

2.6. Measurement of oxygen and nitrogen permeability

Oxygen and nitrogen permeability coefficients (P_{O_2} and P_{N_2}: $cm^3(STP)cm^2/cm \cdot s \cdot cmHg$) and oxygen separation factor ($\alpha = P_{O_2}/P_{N_2}$) were measured by gas chromatographic method using YANACO GTR-10 according to Ref. [5].

2.7. ESR measurement

ESR spectra were taken on a JEOL JES-2XG ESR spectrometer with 100-KHz field modulation in the X-band frequency region. The spin concentrations of each sample were determined by careful double integration of the ESR signal versus standard concentrations of the 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) solution. Signal positions were calibrated against an external standard of Mn^{2+} ($g = 1.981$).

2.8. Other measurements

IR and ^{1}H NMR spectra were measured with a Hitachi IR 270-30 and a Varian Gemini 200H (200 MHz) spectrometer, respectively. Average molecular weights (M_n and M_w) were evaluated by GPC using Hitachi 655A-11 Liquid Chromatograph instruments (polystyrene gel columns (Shodex KF-806L), THF eluent, polystyrene calibration). The optical spectra were measured with a Shimadzu UV-160 spectrometer.

Table 3
Bulk copolymerization of VPHG and VPAcG with TMSSt (80°C, 3 h) or OMA (80°C, 12 h)

M_1	M_2	M_2 in feed (mol%)	$[AIBN]_0/[M_2]_0$ (mol%)	Yield (%)	M_n ($\times 10^4$)[a]	$\bar{M}_w/\bar{M}_n$[a]	M_2 in polymer (mol%)[b]
TMSSt	VPHG	7.7	63	40	7.3	1.4	10
	VPAcG	7.2	69	56	8.9	1.6	11
OMA	VPHG	8.7	48	4	1.9	1.1	0
	VPAcG	8.1	16	4	14	2.1	5.6

[a] Determined from GPC calibrated by polystyrene standard.
[b] Determined from ^{1}H NMR.

Table 4
Bulk copolymerization of MVB with TMSSt ($[\mathrm{AIBN}]_0/[\mathrm{M}]_0 = 0.2$ mol% except for No. 1 (1 mol%), 70°C, 0.5–3 h) and coupling reaction of poly(MVB-TMSSt) with [3,5-di-*tert*-butyl-4-(trimethylsiloxy)phenyl]lithium ([3,5-di-*tert*-butyl-4-(trimethylsiloxy)phenyl]lithium: 10–30 eq.; −70°C, 2 h, and 25°C, 4 h in THF)

Run	Poly(MVB-TMSSt)					Poly(VPHG-TMSSt)					
	MVB in feed (mol%)	Yield (%)	$\bar{M}_n$[a] ($\times 10^5$)	$\bar{M}_w/\bar{M}_n$[a]	MVB in polymer (mol%)[b]	Yield (%)	Composition[b] (MVB/VPHG/TMSSt)	$\bar{M}_n$ ($\times 10^5$)[a]	$\bar{M}_w/\bar{M}_n$[a]	$\bar{P}D_r/\bar{P}D_p$ ($\times 10^3/\times 10^3$)[c,d]	Membrane forming ability[e]
1	100	7	1.6	1.4	100	30	0/100/0	–	–	–	–
2	11	21	1.6	1.7	22	69	0/23/77	2.5	4.0	0.93/1.0	+
3	5.4	14	1.6	3.5	13	42	0/13/87	2.4	5.5	0.92/1.1	++
4	2.0	42	1.2	3.5	3.8	58	0/5.5/94	2.3	5.9	0.68/1.2	++

[a] Determined from GPC calibrated by polystyrene standard.
[b] Determined from ^{1}H NMR.
[c] Degree of polymerization for reacted Poly(MVB-TMSSt) (calculated from $\bar{M}_n$).
[d] Degree of polymerization for produced Poly(VPHG-TMSSt) (calculated from $\bar{M}_n$).
[e] ++, Tough; +, brittle; –, poor.

3. Results and discussion

3.1. Copolymerization of hydrogalvinoxyl monomers

EPHG was copolymerized with TMSPA using $[Rh(C_7H_8)Cl]_2$ in chloroform to yield the corresponding poly(EPHG-TMSPA) as shown in Table 1. EPHG was reported to polymerize with (1,5-cyclooctadiene)chlororhodium(I) dimer catalyst, $[Rh(C_8H_{12})Cl]_2$, but the polymer yield was very low (~4%) due to a very bulky substituent of EPHG at the *para* position [7]. As in experiment $[Rh(C_7H_8)Cl]_2$ catalyst gave much better yield for the polymerization of EPHG, we used this catalyst and obtained the copolymers in a better yield with higher molecular weight ($\bar{M}_n \approx 10^5$). With increasing the composition of the comonomer, TMSPA, the $\bar{M}_n$ of the copolymer increased. Although poly(EPHG) indicated poor solubility in common organic solvents due to the stiff and hindered side-chain structure, poly(EPHG-TMSPA) was more soluble in organic solvents, such as chloroform, benzene and THF in spite of the higher molecular weight. Poly(EPHG-TMSPA) with high EPHG composition was insoluble in hexane and was soluble in methanol due to hydroxyl group of EPHG. This solubility was inverted as the composition of TMSPA was increased, due to trimethylsilyl group of TMSPA. The structure of polymers was confirmed by IR and ^1H NMR spectra; peaks assignable to the ethynyl group of monomers, i.e. δ 3.10 (s, 1H, ≡CH) in ^1H NMR and 3316 cm^{-1} (ν ≡C–H) in IR, completely disappeared, and the sharp absorption at 3635 cm^{-1} (ν(O–H) of the sterically hindered phenolic group and the strong one at 1610–1630 cm^{-1} (νC=O) of quinoid structure remained. The compositions of the copolymers were almost the same as the feed compositions of monomers. The copolymer compositions were determined from ^1H NMR; δ 0.1 (s, 9H, $-Si(CH_3)_3$ of TMSPA) and 1.0–2.0 (br, 36H, $-C(CH_3)_3$ of EPHG). The formation of copolymers was confirmed by the unimodal molecular weight distribution in the GPC curve. Poly(EPHG-TMSPA) indicated good moldability by the solvent-casting method to give clear film with orange color due to hydrogalvinoxyl chromophore. As the composition of TMSPA was increased, poly(EPHG-TMSPA) gave a tougher membrane enough to apply to gas permeation measurement.

VPHG and VPAcG were copolymerized with TMSSt and OMA using AIBN as an initiator in THF to yield the corresponding poly(VPHG-TMSSt), poly(VPAcG-TMSSt), poly(VPHG-OMA) and poly(VPHG-OMA), as shown in Table 2, where OMA was used as one of the acrylate comonomer because the resulting polymer gave good membrane. We have already reported that a large amount of AIBN was needed to polymerize VPHG because radical recombination occurred via the hydrogen abstraction of hydrogalvinoxyl's hydroxyl group [8]. Copolymerization of VPHG also needed a large amount of AIBN, while VPAcG could be polymerized using a smaller amount of AIBN than for VPHG. The compositions of the copolymers were determined from ^1H NMR; δ 0.21 (s, 9H (TMSSt), $-Si(CH_3)_3$) and 1.0–2.0 (br, 39H (VPHG) + 3H (TMSSt), alkyl) for poly(VPHG-TMSSt), 0.21 (s, 9H (TMSSt), $-Si(CH_3)_3$) and 2.38 (s, 3H (VPAcG), CH_3COO-) for poly(VPAcG-TMSSt), 3.82 (s, 2H (OMA), $-CH_2-O-CO-$) and 6.9–7.6 (br, 8H (VPHG), ArH) for poly(VPHG-OMA), and 2.38 (s, 3H (VPAcG), CH_3COO-) and 3.82 (s, 2H (OMA), $-CH_2-O-CO-$) for poly(VPAcG-OMA). The correlation between the monomer composition in feed and that in copolymer in Table 2 suggests that the decreasing order of monomer reactivity is VPAcG ≥ OMA ≥ VPHG ≫ TMSSt.

In order to increase molecular weight of VPHG copolymer, bulk polymerization was attempted as shown in Table 3, because solid VPHG and VPAcG was partially soluble in liquid TMSSt and OMA. The composition of VPHG and VPAcG in the copolymers decreased due to incomplete dissolution of VPHG and VPAcG in comparison with solution polymerization. In general, molecular weight of a polymer obtained by bulk polymerization is larger than that in solution polymerization, and the increased molecular weight was observed in this result as well except for poly(VPHG-OMA). The copolymerization was confirmed by disappearance of peaks assignable to the ethylene unit of the corresponding monomer in IR and ^1H NMR, and by existence of the peaks characterized by side-chain moiety. The formation of copolymers was confirmed by the unimodal molecular weight distribution in GPC curve. Each copolymer was soluble in chloroform, benzene, THF and acetone, and was fabricated by the solvent-casting method to self-supporting membranes with orange color due to hydrogalvinoxyl chromophore, but the membranes were too brittle because of their low molecular weight to apply to the gas permeation measurement.

3.2. Reaction of carboxylate in the polymer with [3,5-di-tert-butyl-4-(trimethylsiloxy)phenyl]lithium

It was reported that [3,5-di-*tert*-butyl-4-(trimethylsiloxy)-phenyl]lithium was coupled with a carboxylate to produce hydrogalvinoxyl structure [9]. Some of the polymers with carboxylate groups, Poly(MMA), Poly(OMA) and Poly(MVB), were treated with [3,5-di-*tert*-butyl-4-(trimethylsiloxy)phenyl]lithium. When each reactant was mixed, the color of the mixture changed into orange due to hydrogalvinoxyl chromophore. But the resulting isolated polymers were white in the case of poly(MMA) and poly(OMA). The GPC indicated degradation of the polymers in the course of the polymer reaction, and ^1H NMR spectra of the polymers showed no peaks in the aromatic region. It was found that the coupling reaction of [3,5-di-*tert*-butyl-4-(trimethylsiloxy)phenyl]lithium with the carboxylate was accompanied by decomposition of the polymer chain. On the contrary, the carboxylate of poly(MVB) was completely converted to hydrogalvinoxyl unit by using ca. 10 times

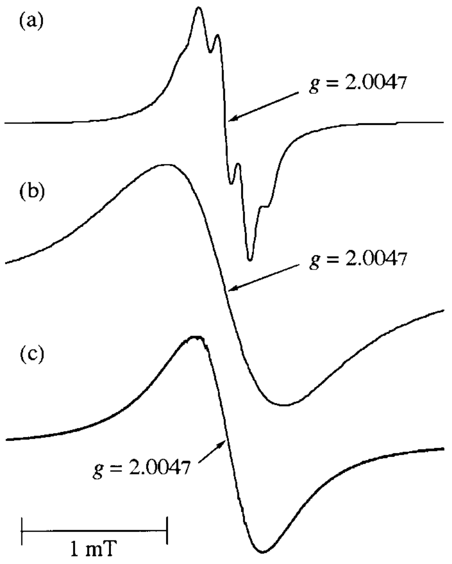

Fig. 1. ESR spectra of the poly(VPG-TMSSt) (prepared from No 2 in Table 4) at room temperature with: (a) 0.44 spin/unit in benzene; (b) 0.46 spin/unit in the membrane state; and (c) of the poly(EPG-TMSPA) (prepared from No 4 in Table 1) with 0.48 spin/unit in the membrane state.

larger molar amount of [3,5-di-*tert*-butyl-4-(trimethylsiloxy)-phenyl]lithium to the carboxylate. The reaction was confirmed by the change in IR spectrum; disappearance of 1730 cm^{-1} (ν C=O) due to the carbonyl group of the carboxylate, and appearance of 3635 cm^{-1} (ν O–H) and 1610–1630 cm^{-1} (ν C=O) due to the hydroxyl group and the quinoid structure of hydrogalvinoxyl unit, respectively.

Poly(MVB-TMSSt) was also treated with [3,5-di-*tert*-butyl-4-(trimethylsiloxy)phenyl]lithium to give poly(VPHG-TMSSt). Poly(MVB-TMSSt) was obtained by copolymerization of MVB and TMSSt as shown in Table 4. The formation of copolymers was confirmed by the unimodal molecular weight distribution in GPC curve. The compositions of the copolymers were determined from ^{1}H NMR; δ 0.2 (s, 9H, $-\mathrm{Si(CH_3)_3}$ of TMSSt) and 3.9 (s, 3H, $-\mathrm{COOCH_3}$ of MVB). MVB composition in the copolymers was twice higher than that in the feed, which suggests that the monomer reactivity of MVB was higher than that of TMSSt. The conversion of carboxylates and the composition of copolymers were determined from ^{1}H NMR; δ 0.2 (s, 9H (TMSSt), $-\mathrm{Si(CH_3)_3}$), 1.0–2.0 (br, 39H (VPHG) + 3H (TMSSt) + 3H (MVB), alkyl) and 3.9 (s, 3H (MVB), $-\mathrm{COOCH_3}$). The complete conversion from poly(MVB-TMSSt) to poly(VPHG-TMSSt) was confirmed from ^{1}H NMR and IR spectra; disappearance of peaks assignable to the carboxylate, i.e. δ 3.9 (s, 3H, $-\mathrm{COOCH_3}$) in ^{1}H NMR and 1730 cm^{-1} (ν C=O) in IR, and appearance of peaks assignable to hydrogalvinoxyl unit, i.e. δ 1.3 (s, 36H, $-\mathrm{C(CH_3)_3}$) and 5.5 (s, 1H, –OH) in ^{1}H NMR, and 1610 (ν(C=O), 2964 (ν($-\mathrm{C(CH_3)_3}$), 3635 cm^{-1} (ν(O–H) in IR spectrum. The molecular weight of poly(VPHG-TMSSt) increased compared with that of the starting poly(MVB-TMSSt), and this increment agreed with the molecular weight corresponding to the composition of hydrogalvinoxyl unit. The synthesis of poly(VPHG-TMSSt) from poly(MVB-TMSSt) led to success in attaining higher molecular weight of poly(VPHG-TMSSt) in comparison with poly(VPHG-TMSSt) obtained from the copolymerization of VPHG with TMSSt described above, and the poly(VPHG-TMSSt) gave tougher membrane enough to apply to the gas permeation measurement.

3.3. Chemical oxidation of hydrogalvinoxyls

Poly(EPHG-TMSPA) and poly(VPHG-TMSSt) gave corresponding polyradicals, poly(EPG-TMSPA) and poly(VPG-TMSSt), respectively, by chemical oxidation using fresh $\mathrm{PbO_2}$ or alkaline $\mathrm{K_3Fe(CN)_6}$ in an oxygen-free atmosphere. The hydrogalvinoxyl units of poly(EPHG-TMSPA) and poly(VPHG-TMSSt) in solution were efficiently converted into galvinoxyl radicals by treatment with either of the oxidizing agents. The reaction was confirmed by disappearance or decrease of the peak assignable to the hydroxyl group of hydrogalvinoxyl, i.e. 3635 cm^{-1} (ν O–H) in IR spectrum, and by decrease of visible absorption maxima at 410–420 nm attributed to hydrogalvinoxyl chromophore and appearance at 470 nm because of the galvinoxyl radical. GPC curves of the polyradicals were almost the same as those of corresponding hydroxyl polymers, e.g. $\bar{M}_\mathrm{n} = 1.3 \times 10^5$ and $\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n} = 2.9$ for poly(VPHG-TMSSt) (No. 2 in Table 4). These findings supported that oxidation did not bring about oxidative degradation or cross-linking of the main chains. The polyradicals were fabricated to self-supporting membranes with brown color due to galvinoxyl radical chromophore by the solvent-casting method in an oxygen-free atmosphere. Although the membranes of polyradicals were less tough than that of corresponding hydrogalvinoxyl polymers, some of them were durable enough to apply to the gas permeation measurement.

3.4. ESR spectra and stability of galvinoxyls

In the ESR spectra of the polyradical solutions, a hyperfine structure was observed at a *g*-value of 2.0047 with a relative signal intensity of 1:4:6:4:1 attributed to the magnetic interaction of an unpaired electron with four equivalent protons of a galvinoxyl unit, e.g. for poly(VPG-TMSSt) as shown in Fig. 1a. On the other hand, the ESR spectra of the polyradical membranes gave no hyperfine structure due to exchange coupling between polyradicals, and only single broad signal was observed at a *g*-value of 2.0047 as shown in Fig. 1b and c. The ESR peak-to-peak line width (ΔH_pp) of the polyradical membranes was 0.46 mT for poly(EPG-TMSPA) and 0.81 mT for poly(VPG-TMSSt), respectively, at around room temperature, whose ΔH_pp values were similar to that of the previously reported homo-polyradicals [7,8] with low spin concentration (0.1–0.2 spin/unit). This result indicated that the diamagnetic comonomers, TMSPA and TMSSt, played

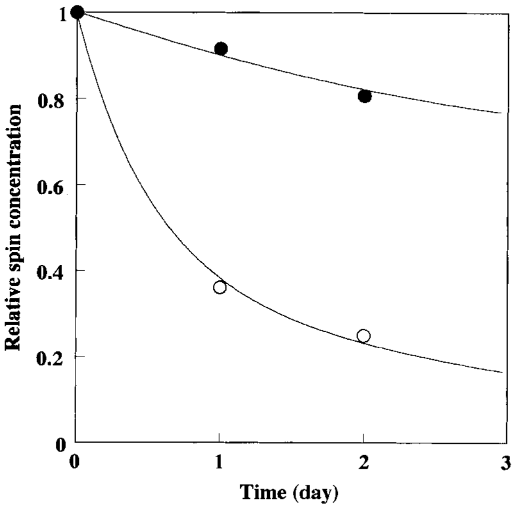

Fig. 2. Time dependence of the spin concentration for poly(VPG-TMSSt) (prepared from No 2 in Table 4) (○) in benzene and (●) in membrane state under atmospheric conditions.

a role to dilute radical units along the polyradical chain, because the ΔH_{pp} of homo-polyradicals increased with decrease of spin concentration. The spin concentration of polyradicals reached up to ca. 0.6 spin/unit depending on the oxidation conditions. The polyradical membranes were much stable even under atmospheric conditions in comparison with the solution states where half-life of the spin concentration was ca. 19 h under atmospheric conditions as shown in Fig. 2. It was found that the polyradical membrane was stable enough to maintain the initial spin concentration under the conditions of the following gas permeation measurement.

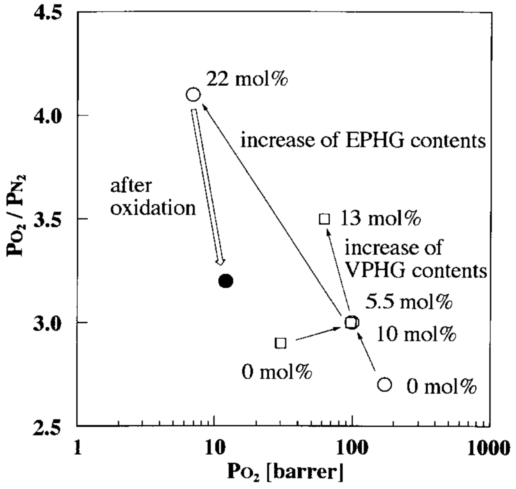

Fig. 3. Oxygen permselectivity of: (○) poly(EPHG-TMSPA) (0, 10 and 22 mol% galvinoxyl unit); (●) poly(EPG-TMSPA) (22 mol% galvinoxyl unit with 0.48 spin/unit); and (□) poly(VPHG-TMSSt) (0, 5.5 and 13 mol% galvinoxyl unit) membranes. Poly(TMSPA) from Ref. [5], and poly(TMSSt) from Ref. [6].

3.5. Oxygen permeation behavior

Oxygen and nitrogen permeation properties were measured using air as feed gas at 298 K and 76 cmHg for the polymer and polyradical membranes (Nos. 4 and 5 in Table 1, and Nos. 3 and 4 in Table 4). Fig. 3 shows the relationship between the oxygen permeability coefficient (P_{O_2}) and the oxygen separation factor ($\alpha = P_{O_2}/P_{N_2}$) for the polymer and polyradical membranes. The α values of polymers containing galvinoxyl units were higher, while the P_{O_2} values were lower. This result was caused by modification of the micro structure of membranes by the galvinoxyl units, i.e. the membranes became denser and harder with increase in the galvinoxyl unit, in comparison with poly(TMSPA) or poly(TMSSt) homopolymer. Enhancement of α was not observed in case of poly(EPG-TMSPA), though it was expected that the enhancement in α was caused by interaction between the oxygen radical unit in membranes and unpaired electrons of oxygen molecules as a permeant.

4. Conclusions

EPHG was polymerized using $[Rh(C_7H_8)Cl]_2$ to give corresponding poly(EPHG), and its copolymers with TMSPA were obtained with very high molecular weight. Poly(VPHG-TMSSt)s with high molecular weight were synthesized by the polymer reaction of poly(MVB-TMSSt) with [3,5-di-*tert*-butyl-4-(trimethylsiloxy)phenyl]lithium. The hydrogalvinoxyl polymers were converted to the corresponding polyradicals by chemical oxidation. These copolymers and polyradicals containing galvinoxyl units exhibited good moldability because of introduced trimethylsilyl groups, and could be successfully fabricated to self-supporting membranes with orange and brown color, respectively. The polyradical membranes were so stable that the initial spin concentration was maintained for a few days. It was found that the copolymer membranes containing galvinoxyl units enhanced the permselectivity of oxygen to nitrogen in comparison with the corresponding homopolymer, poly(TMSPA) and poly(TMSSt).

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References

[1] Coppinger GM. A stable phenoxy radical inert to oxygen. J Am Chem Soc 1957;79:501–2.

[2] Forrester AR, Hay JM, Thomson RH. Organic chemistry of stable free radicals, New York: Academic Press, 1968 and references therein.

[3] Braun D. Polyradicals. In: Bikales NM, editor. Encyclopedia of polymer science and technology, 15. New York: Interscience, 1971. pp. 429–44 and references therein.

[4] Nishide H. High-spin alignment in π-conjugated polyradicals: a magnetic polymer. Adv Mater 1995;7(11):937–41 and references therein.

[5] Aoki T, Nakahara H, Hayakawa Y, Kokai M, Oikawa E. Trimethylsilyl-group containing polyphenylacetylenes for oxygen and ethanol permselective membranes. J Polym Sci Polym Chem Ed A 1994;32(5):849–58.

[6] Kawakami Y, Karasawa H, Aoki T, Yamamura Y, Hisada H, Yamashita Y. Polymers with oligoorganosiloxane side chains as materials for oxygen permeable membranes. Polym J 1985;17(11):1159–72.

[7] Yoshioka N, Nishide H, Kaneko T, Yoshiki H, Tsuchida E. Poly[(*p*-ethynylphenyl)hydrogalvinoxyl] and its polyradical derivative with high spin concentration. Macromolecules 1992;25(15):3838–42.

[8] Kaneko T, Tatsumi H, Aoki T, et al. Polymerization of (*p*-vinylphenyl)hydrogalvinoxyl and formation of a stable polyradical derivative. J Polym Sci Polym Chem Ed A 1999;37(2):189–98.

[9] Harrer W, Kurreck H, Reusch J, Gierke W. Über galvinole und galvinoxyl-mehrspinsysteme I. Tetrahedron 1975;31:625–32.