Influence of Side-Chain Length on the Gas Permeation Properties of Poly(2-alkylacetylenes)[†]

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ABSTRACT: The pure-gas permeation properties for a systematic series of disubstituted, amorphous, glassy poly(2-alkylacetylenes), i.e., poly(2-hexyne), poly(2-octyne), poly(2-nonyne), poly(2-decyne), and poly(2-undecyne), were determined at 35 °C for H_2, CO_2, O_2, N_2, CH_4, C_2H_6, C_3H_8, and n-C_4H_{10}. Gas permeability increased by increasing the (i) side-chain length of the polymers and (ii) size and condensability of the penetrants. For example, the nitrogen and *n*-butane permeabilities of poly(2-undecyne) were 2- and 10-fold higher than those of poly(2-hexyne). As the fractional free volume decreases with increased side-chain length, the permeability increases. This behavior is opposite to that observed in polyacetylenes containing terminal bulky side-group substituents, such as trimethylsilyl or isopropyl groups. In branched acetylene-based polymers, the gas permeation properties correlate well with their free volume values; as fractional free volume increases, a simultaneous increase in permeability is observed. In linear poly(2-alkylacetylenes), an increase in side-chain length increases the overall chain mobility and increases the chain packing density of the polymers. In mixed-gas permeation experiments, an increase in mixed-gas *n*-butane permeability and *n*-butane/methane selectivity was observed with increasing side-chain length of poly(2-alkylacetylenes).

Introduction

Polyacetylene-based polymers have been studied extensively in the past decade for membrane-based gas- and vapor-separation applications. These amorphous, highly rigid, glassy polymers are characterized by high glass transition temperatures, typically >200 °C, low densities, high fractional free volume, and very high gas permeabilities. In particular, poly(1-trimethylsilyl-1-propyne) [PTMSP] and poly(4-methyl-2-pentyne) [PMP] have the highest gas permeabilities of all known polymers.[1−4] In contrast to conventional glassy polymers, high free volume polyacetylenes are significantly more permeable to large organic vapors than to small permanent gases.[5,6] The unique permeation characteristics of PTMSP and PMP result from very poor polymer chain packing because of the stiffness of the polymer chains, which is caused by the alternating double bonds along the main chain and short, bulky side-chain substituents.[4,5,7,8]

Previously, the effects of pendant side chains on the gas permeation properties of a variety of polymers, such as polynorbornenes, poly(alkylphosphazenes), and poly(alkyl acrylates), were investigated.[9−11] A clear trend of the influence of side-chain length on gas permeability was not observed for these different types of polymers. On the basis of previous studies, the gas permeability of polymers can either increase[10,11] or decrease[9,12,13] with increasing side-chain length, depending on the structural configuration of the main chain relative to that of the pendant side group. In some rare cases, the gas permeability is essentially not affected by changes in side-chain pendant group.[14] To date, only a few systematic studies have investigated the effects of the side-chain length of substituted polyacetylenes on their gas permeation properties, and a clear trend has not been observed.[9−14] In this paper, we report on the influence of the side-chain length on the pure- and mixed-gas permeation properties for a series of systematically modified poly(2-alkylacetylenes).

Experimental Section

Polymer Synthesis. The monomers 2-pentyne, 2-hexyne, and 2-octyne were purchased from GFS Chemicals (Powell, OH); 2-nonyne, 2-decyne, and 2-undecyne were purchased from Lancaster Synthesis, Inc. (Windham, NH). Polymerization was carried out by a procedure similar to that reported by Higashimura et al.[15] The catalysts, $MoCl_5$ and Ph_4Sn, were purchased from Strem Chemicals, Inc. (Newburyport, MA), and used without further purification. A solution of 120 mM $MoCl_5$ and 120 mM Ph_4Sn in toluene was stirred at room temperature for 10 min under dry nitrogen. Thereafter, the monomer was added dropwise to the catalyst solution, and the mixture was reacted for 2 h at room temperature. The monomer concentration in the mixture was 2 mol/L. The temperature and the viscosity of the solution increased rapidly. The viscous solution was diluted with toluene and poured into a large amount of methanol, filtered to recover the precipitated polymer, and dried under vacuum. The polymers were dissolved in toluene and reprecipitated twice from methanol to remove excess monomer, oligomers, and excess catalysts. The yields were about 30−80%. The polymer structures and polymerization yields are summarized in Table 1. As previously reported, poly(2-alkylacetylenes) are amorphous, glassy polymers and have glass transition temperatures ranging from 160 °C for poly(2-decyne) to 200 °C for poly(2-hexyne), as shown in Table 2.[16] As expected, the glass transition temperature decreases by increasing the pendant alkyl side group because of increased side-chain flexibility. This is further reflected in the mechanical properties of the polymers; that is, an increase in side-chain length makes the polymers softer and more ductile, as indicated by a significant decrease in Young's modulus (Table 2).

Polymer Film Preparation. Poly(2-alkylacetylenes) are soluble in many nonpolar organic solvents, such as toluene, hexane, and cyclohexane. Only poly(2-pentyne) was insoluble

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[†] This paper is dedicated to Emeritus Professor Tsutomu Nakagawa of Meiji University, Japan, in honor of his contributions to polymer and membrane science.

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Table 1. Polymer Structures and Polymerization Yields of Poly(2-alkylacetylenes)

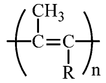 $\left(-C(CH_3)=C(R)- \right)_n$		polymerization yield (%)
polymer	R	
poly(2-pentyne)	C_2H_5	70
poly(2-hexyne)	C_3H_7	50
poly(2-octyne)	C_5H_{11}	44
poly(2-nonyne)	C_6H_{13}	50
poly(2-decyne)	C_7H_{15}	80
poly(2-undecyne)	C_8H_{17}	27

Table 2. Physical Properties of Poly(2-alkylacetylenes)

polymer	T_g[a] (°C)	E[a] (MPa)	density (g/cm^3)	FFV (cm^3/cm^3 polymer)
poly(2-hexyne)	200	970		
poly((2-octyne)	180	830	0.84	0.22
poly(2-nonyne)			0.86	0.20
poly(2-decyne)	160	260	0.87	0.19
poly(2-undecyne)				

[a] Data from ref 16. E = Young's modulus.

in any common organic solvent. Isotropic, dense films of poly(2-alkylacetylenes) were prepared by a ring-casting method from cyclohexane solution (2 wt %) onto a glass plate. The films were dried at ambient conditions for 48 h and then under vacuum at 80 °C for at least 1 day to completely remove the solvent. The thickness of the films was determined with a precision micrometer. Film samples with thicknesses of 40−60 μm ($\pm$0.5 μm) were used for the permeation measurements.

Polymer Density and Fractional Free Volume. The densities of poly(2-octyne) [P2O], poly(2-nonyne) [P2N], and poly(2-decyne) [P2D] were determined gravimetrically by weighing film samples of known area on a microbalance and by measuring their thickness with a precision digital micrometer. The polymer densities were determined on three duplicate films of each polymer type. The densities of P2O, P2N, and P2D were 0.84 ± 0.005, 0.86 ± 0.005, and 0.87 ± 0.005 g/cm^3, respectively. The fractional free volume (FFV) is often used as a relative measure that links the gas permeability in polymers to their chain packing density. The FFV values of the three poly(2-alkylacetylenes), listed in Table 2, were calculated on the basis of measured density and van Krevelen's group contribution method.[17] The FFV values for P2O, P2N, and P2D were 0.22, 0.20, and 0.19, respectively. FFV decreases with increasing linear alkyl side-chain length, indicating higher chain packing density. This result is similar to that recently reported for a systematic series of poly(alkylacetylenes) containing a bulky, terminal isopropyl group in the side chain.[18] The FFV values in poly(2-alkylacetylenes) are similar to those reported for conventional glassy polymers (FFV ~ 0.16−0.22).[19] However, the FFV values in linear poly(alkylacetylenes) are significantly lower than those of polyacetylenes containing short, bulky side groups, such as PMP (FFV = 0.28) and PTMSP (FFV = 0.29).

Characterization of Gas Permeation Properties. The permeability of poly(2-alkylacetylene) films to hydrogen, carbon dioxide, nitrogen, oxygen, methane, ethane, propane, and *n*-butane was determined at 35 °C using the constant pressure/variable volume method. The feed pressure was 50 psig, except for *n*-butane (10 psig); the permeate side pressure was atmospheric (0 psig). Gas permeability based on the constant pressure/variable volume method is given by

$$J = \frac{273.15 p_a}{76 T A (p_2 - p_1)} \left(\frac{dV}{dt} \right) \tag{1}$$

$$P = J l \tag{2}$$

where J is the permeate flux (cm^3 (STP)/(cm^2 s)), P is the gas permeability (cm^3 (STP) cm/(cm^2 s cmHg)), p_a is the atmospheric pressure (cmHg), l is the membrane thickness (cm), T is the gas temperature (K), A is the membrane area (cm^2), p_2 and p_1 are the feed and permeate pressure (cmHg), respectively, and dV/dt is the steady-state rate of displacement of a soap bubble in a flowmeter.

The permeation properties of poly(2-alkylacetylenes) were also determined with binary *n*-butane/methane mixtures (*n*-butane feed concentration: 1−8 mol %) using the constant pressure/variable volume method at 25 °C. The feed pressure was 150 psig; the permeate pressure was atmospheric (0 psig). The stage cut, that is, the ratio of permeate flow rate to feed flow rate, was less than 1%. Because the stage cut was very low, the residue concentration was essentially equal to the feed concentration. The compositions of feed, residue, and permeate were determined with a gas chromatograph equipped with a thermal conductivity detector. The mixed-gas permeability coefficient, P_{mixture}, of each gas component was calculated from the relationship

$$P_{\text{mixture}} = \frac{x_{\text{perm}} J l}{(p_{\text{feed}} x_{\text{feed}}) - (p_{\text{perm}} x_{\text{perm}})} \tag{3}$$

where x_{perm} and x_{feed} are the mole fractions of the gas components in the permeate and feed streams, respectively, and p_{feed} and p_{perm} are the pressures (cmHg absolute) on the feed and permeate side of the membrane, respectively. The mixed-gas selectivity was calculated with the ratio of the permeability coefficients of gas A and gas B.

Results and Discussion

Pure-Gas Permeation Properties. The pure-gas permeabilities of poly(2-alkylacetylenes) are summarized in Table 3. Similar to the permeation behavior of high free volume, branched polyacetylenes,[4−6] permeabilities of poly(2-alkylacetylenes) to large, condensable gases, such as *n*-butane, are higher than those to small, permanent gases, such as methane. This trend is opposite to that observed for conventional, low free volume glassy polymers, such as polyimides; i.e., permeability typically decreases as the size and condensability of the penetrants increase.[20]

The permeabilities in linear poly(2-alkylacetylenes) are significantly lower than those of branched polyacetylenes. For example, the nitrogen permeability at 35 °C of poly(4-methyl-2-pentyne) (PMP) is 1250×10^{-10} cm^3 (STP) cm/(cm^2 s cmHg),[18] whereas that of poly(2-hexyne) is only 12×10^{-10} cm^3(STP) cm/(cm^2 s cmHg). The 100-fold reduction in nitrogen permeability in poly(2-hexyne) relative to that of PMP results from differences in polymer chain packing. It appears that the branched isopropyl side group in PMP, directly attached to the rigid −C=C− main chain, severely hinders efficient molecular chain packing, as indicated by its very high FFV of 0.28. Poly(2-hexyne), on the other hand, containing a linear *n*-propyl side group, apparently exhibits much more efficient overall polymer chain packing and as a result much lower permeability.

The permeability for each gas (except hydrogen) increased with increasing the length of the linear alkyl side chain, as shown in Figures 1 and 2. For example, the propane permeability of poly(2-undecyne) is 20-fold higher than that of poly(2-hexyne). This increase in gas permeability becomes much more pronounced as the size of the penetrant increases. Figure 3 shows the ratio of the permeability for various gases in poly(2-alkylacetylenes) containing *n*-pentyl [poly(2-octyne)] or *n*-octyl [poly(2-undecyne)] side chains relative to that having a *n*-propyl side chain [poly(2-hexyne)] as a function of critical gas volume, which is a relative measure of gas size. The data clearly indicate that an increase in alkyl

Table 3. Gas Permeabilities of Poly(2-alkylacetylenes) at 35 °C and 50 psig

	permeability (10^{-10} cm^3(STP) cm/(cm^2 s cmHg))							
polymer	H_2	CO_2	O_2	N_2	CH_4	C_2H_6	C_3H_8	n-C_4H_{10}[a]
poly(2-hexyne)	160	120	39	12	21	16	35	440
poly(2-octyne)	150	200	57	21	51	99	420	2100
poly(2-nonyne)	140	230	60	23	64	138	450	1850
poly(2-decyne)	150	290	74	29	84	220	740	4600
poly(2-undecyne)	140	290	71	29	83	240	840	3900

[a] Feed pressure: 10 psig.

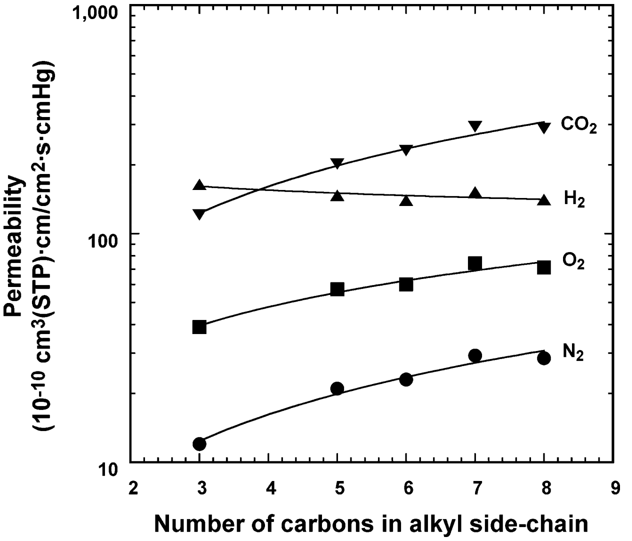

Figure 1. Permeabilities of nitrogen, oxygen, hydrogen, and carbon dioxide in poly(2-alkylacetylenes) as a function of carbon side-chain number.

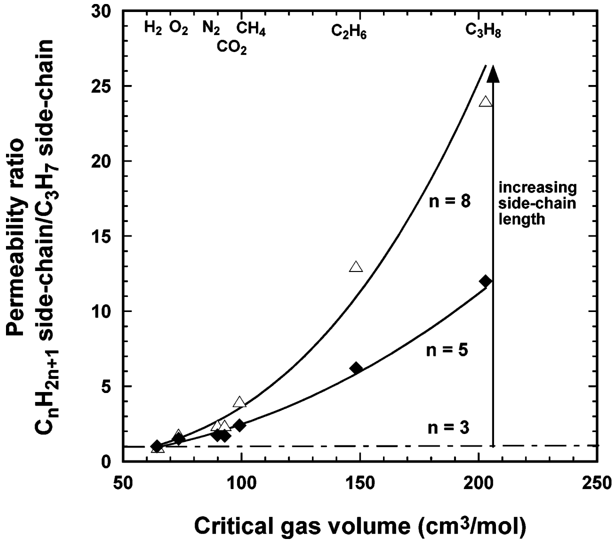

Figure 3. Influence of side-chain length on gas permeability ratio of poly(2-undecyne) [$n = 8$] and poly(2-octyne) [$n = 5$] relative to poly(2-hexyne) [$n = 3$].

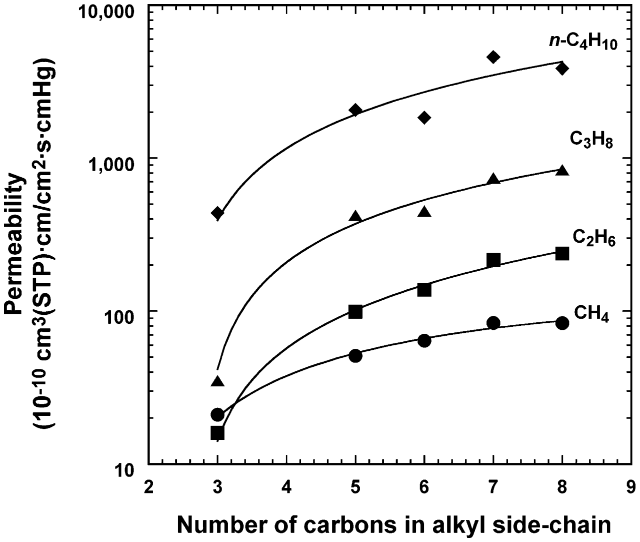

Figure 2. Permeabilities of methane, ethane, propane, and n-butane in poly(2-alkylacetylenes) as a function of carbon side-chain number.

side-chain length results in a significant increase in gas permeability. It is suggested that the increase in permeability was primarily caused by an increase in the diffusion coefficient of the gases because an increase in pendant side-chain length increases the overall chain mobility in poly(2-alkylacetylenes). The only exception to this general trend was observed for hydrogen, the smallest penetrant used in this study. The hydrogen permeability was essentially constant for all poly(2-alkylacetylenes), regardless of side-chain length. It is suggested that an increase in side-chain length had only a very small effect on the diffusion coefficient of hydrogen, which resulted in relatively constant hydrogen permeability.

Our results are in stark contrast to previous studies on the effects of alkyl side-chain length on gas permeability in other polyacetylenes. Specifically, in branched polyacetylenes, such as poly(silylpropynes)[12,13] and isopropyl-terminated poly(2-alkylacetylenes),[18] gas permeability decreases dramatically by increasing the alkyl side-chain length. For poly(2-alkylacetylenes) containing a terminal branched side chain, the reduction in permeability correlates well with fractional free volume; i.e., an increase in side-chain length leads to lower FFV and, therefore, lower gas permeability.[13,18] It is important to note that polyacetylenes containing bulky side groups directly connected to the $-C{=}C-$ main chain show extremely high gas permeability due to (i) very high free volume, (ii) large interchain spacing, and (iii) connectivity of free volume elements.[3,5] This results from severely hindered chain packing due to the very rigid $-C{=}C-$ main chain and the bulky side group. On the other hand, if an alkyl side group is attached to the main chain and is terminated with a bulky side group, the polymer chains can pack much more efficiently due to the increased mobility of the alkyl side-chain spacer group.[13,18]

In the linear poly(2-alkylacetylenes) of this study the fractional free volume decreased with increasing alkyl side-chain length; however, this was coupled with an increase in gas permeability. This result is unexpected as the permeability for a systematic series of polymers typically correlates fairly well with fractional free volume. It is suggested that chain mobility in linear poly(2-alkylacetylenes) contributes more significantly to gas permeability than fractional free volume. Because

Table 4. Gas/Nitrogen Selectivities of Poly(2-alkylacetylenes) at 35 °C and 50 psig

polymer	gas/nitrogen selectivity						
	H_2	CO_2	O_2	CH_4	C_2H_6	C_3H_8	n-C_4H_{10}[a]
poly(2-hexyne)	13	10	3.3	1.8	1.3	2.9	37
poly(2-octyne)	7	10	2.7	2.4	4.7	20	100
poly(2-nonyne)	6	10	2.6	2.8	6.0	20	80
poly(2-decyne)	5	10	2.6	2.9	7.6	26	160
poly(2-undecyne)	5	10	2.5	2.9	8.3	29	140

[a] Feed pressure: 10 psig.

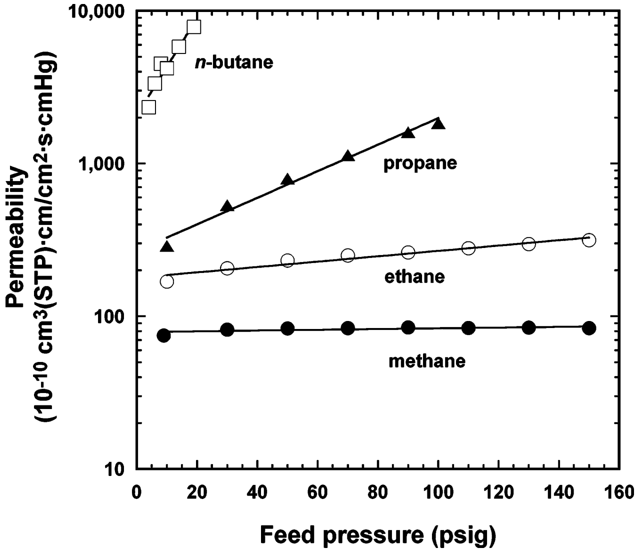

Figure 4. Permeability of methane, ethane, propane, and *n*-butane in poly(2-undecyne) as a function of feed pressure.

of increased side-chain mobility in longer-chain poly-(2-alkylacetylenes), it seems reasonable to assume that the diffusion coefficients of the gases increased, leading to the observed increase in permeability.

The gas/nitrogen selectivities of the poly(2-alkylacetylenes) are shown in Table 4. It is noteworthy that polymers containing C_5-C_8 alkyl side chains have relatively similar selectivities. This trend has been observed in earlier work.[8] On the other hand, poly(2-hexyne), which has the shortest side chain in this series of polymers and the lowest permeabilities, exhibits higher O_2/N_2 and H_2/N_2 selectivities but significantly lower hydrocarbon/nitrogen selectivities relative to those of the other polymers. On the basis of pure-gas measurements, C_5-C_8 side-chain poly(2-alkylacetylenes) have very high hydrocarbon/methane selectivities. For example, poly(2-undecyne) showed pure-gas propane/methane and *n*-butane/methane selectivities of 10 and 47, respectively. However, these pure-gas selectivity values severely overestimate the selectivity obtained in gas mixtures containing hydrocarbons at relatively low vapor activity, as discussed below.

Figure 4 shows the pressure dependence of gas permeation in poly(2-undeyne) for a series of hydrocarbons at 35 °C. The permeability of the least condensable gas, i.e., methane, is essentially independent of feed pressure. However, as the condensability of the hydrocarbon gases increases, the permeability increases significantly with pressure. For example, the propane permeability increased about 6-fold from 290×10^{-10} cm^3 (STP) cm/(cm^2 s cmHg) at 10 psig (relative propane pressure = 0.14) to 1850×10^{-10} cm^3 (STP) cm/(cm^2 s cmHg) at 110 psig (relative propane pressure = 0.71). This increase in permeability is caused by enhanced sorption of the more condensable hydrocarbons in the polymer, leading to increased chain mobility and, hence, increased diffusivity and permeability.

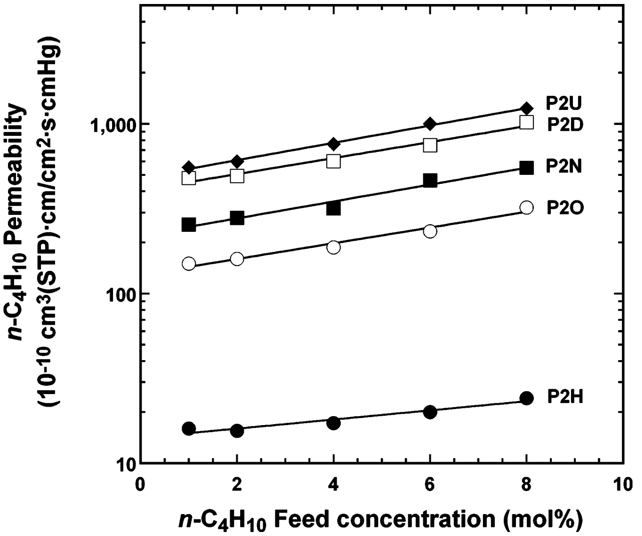

Figure 5. Mixed-gas *n*-butane permeability in poly(2-alkylacetylenes) as a function of *n*-butane feed concentration. Feed pressure: 150 psig; permeate pressure: atmospheric (0 psig); temperature: 25 °C. The *n*-butane relative pressures (p/p_{sat}) were 0.05, 0.1, 0.2, 0.3, and 0.4 for *n*-butane feed concentrations of 1, 2, 4, 6, and 8 mol %, respectively.

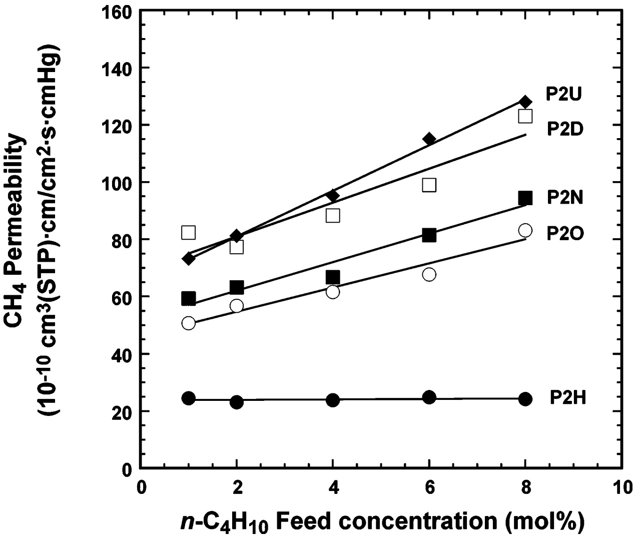

Figure 6. Mixed-gas methane permeability in poly(2-alkylacetylenes) as a function of *n*-butane feed concentration. Feed pressure: 150 psig; permeate pressure: atmospheric (0 psig); temperature: 25 °C. The *n*-butane relative pressures (p/p_{sat}) were 0.05, 0.1, 0.2, 0.3, and 0.4 for *n*-butane feed concentrations of 1, 2, 4, 6, and 8 mol %, respectively.

Mixed-Gas Permeation Properties. The gas permeation properties of poly(2-alkylacetylenes) were also determined with *n*-butane/methane mixtures. Figure 5 shows *n*-butane permeabilities of poly(2-alkylacetylenes) as a function of the *n*-butane feed concentration. The permeability of *n*-butane increases for all poly(2-alkylacetylenes) as the concentration of *n*-butane increases in the feed. The increase in *n*-butane permeability was caused by swelling of the polymer, as indicated by a simultaneous increase in the mixed-gas methane permeability, as shown in Figure 6. However, the relative increase in *n*-butane permeability is larger than that of methane, as shown in Figure 7. As typically observed in polymer membranes for the separation of

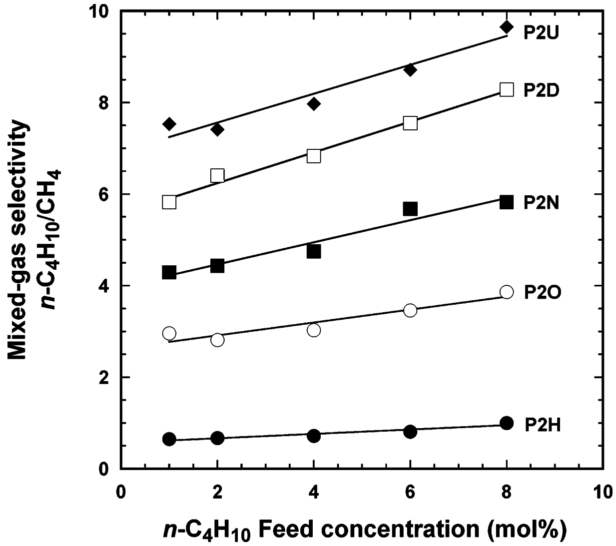

Figure 7. Mixed-gas *n*-butane/methane selectivity of poly(2-alkylacetylenes) as a function of *n*-butane feed concentration. Feed pressure: 150 psig; permeate pressure: atmospheric (0 psig); temperature: 25 °C. The *n*-butane relative pressures (p/p_{sat}) were 0.05, 0.1, 0.2, 0.3, and 0.4 for *n*-butane feed concentrations of 1, 2, 4, 6, and 8 mol %, respectively.

large, organic vapors from small, permanent gases, swelling always leads to an increase in organic-vapor/permanent-gas selectivity. This behavior occurs because swelling enhances polymer chain mobility, which results in a larger increase in the diffusion coefficient of the large organic vapor relative to that of a small permanent gas.

The mixed-gas permeation behavior in linear poly(2-alkylacetylenes) is quite different from that observed in high free volume, branched polyacetylenes, such as PTMSP and PMP. In branched polyacetylenes, the permeabilities of permanent gases, such as methane, are typically reduced by copermeation of condensable feed gas components, such as *n*-butane.[5,21,22] As a result, the selectivity obtained in mixed-gas permeation experiments is significantly higher than that predicted from pure-gas measurements. In polymeric materials, this permeation behavior has only been observed in ultrahigh free volume polyacetylenes. On the other hand, the same transport mechanism occurs in nanoporous inorganic materials having pore sizes of less than about 20 Å.[23] The similar structural properties of PTMSP and nanoporous inorganic materials, such as silica gels, have been confirmed by positron annihilation spectroscopy.[24] It has been postulated that a large fraction of free volume elements in PTMSP and PMP are interconnected with average interchain spacing larger than the dimensions of the penetrants.[5,22] Therefore, it is suggested that the different mixed-gas permeation properties of linear alkyl-based and branched alkyl-based polyacetylenes probably result from differences in free volume, free volume element size, free volume distribution, and polymer chain mobility.

The *n*-butane/methane selectivities of the poly(2-alkylacetylenes) increase as the length of the side chain increases, as shown in Figure 7. For a gas mixture containing 2 mol % *n*-butane in methane, the $n\text{-}C_4H_{10}/CH_4$ selectivity of poly(2-alkylacetylenes) increased from 0.6 for poly(2-hexyne) [*n*-propyl side chain] to 7 for poly(2-undecyne) [*n*-octyl side chain]. In addition, the $n\text{-}C_4H_{10}/CH_4$ selectivity of the linear poly(2-alkylacetylenes) increased as the *n*-butane concentration increased in the feed. This result is expected because swelling in rubbery as well as glassy polymers leads to a more significant increase in the diffusion coefficient of the larger penetrant (*n*-butane) as compared to that of the smaller molecule (methane). This leads to a larger increase in *n*-butane permeability relative to that of methane and, hence, an increase in selectivity. On the other hand, in ultrahigh free volume, branched polyacetylenes, such as PTMSP or PMP, an increase in *n*-butane/methane selectivity occurs due to blocking of the less condensable gas (methane) by copermeation of a highly sorbing vapor (*n*-butane).[5,21]

In the separation of small permanent gases, where the smaller penetrant is the preferentially permeating component, a tradeoff relationship between permeability and selectivity has been noted, that is, polymers that exhibit high permeability typically have low selectivity and vice versa.[25] For example, this permeability/selectivity tradeoff relationship has been observed for O_2/N_2, H_2/N_2, and CO_2/CH_4 separation.

On the other hand, in the separation of large, organic vapors from small permanent gases, an inverse permeability/selectivity relationship exists; i.e., membranes that exhibit the highest organic vapor permeability also have the highest organic-vapor/gas selectivity.[18,26] It is important to note that this inverse permeability/selectivity relationship occurs only in mixtures in which the larger penetrant is the faster permeating component. The overall selectivity, $\alpha_{vapor/gas}$, can be factored into the solubility selectivity, S_{vapor}/S_{gas}, and the diffusivity selectivity, D_{vapor}/D_{gas}. In general, organic vapors exhibit significantly higher solubility than permanent gases in a polymer; consequently, S_{vapor}/S_{gas} is typically much larger than one. On the other hand, the large vapor will always have a lower diffusion coefficient than the smaller penetrant. Hence, the diffusivity selectivity, D_{vapor}/D_{gas}, will always be less than one. As a result, D_{vapor}/D_{gas} will always reduce the overall selectivity, $\alpha_{vapor/gas}$, in polymeric materials used for the separation of vapors from gases. Therefore, advanced membranes for organic-vapor/gas separation, which have both increased permeability as well as higher selectivity, require materials that exhibit the smallest difference in diffusion coefficient between the organic vapor and the gas as possible. Such advanced materials can be based on rubbery polymers that have extremely high chain flexibility, such as poly(dimethylsiloxane), or on ultrahigh free volume polymers having very large free volume and connectivity of free volume elements, such as PTMSP or PMP.

An example of the permeability/selectivity relationship for organic-vapor/gas separation is shown in Figure 8 for *n*-butane/methane separation. The data were collected for a series of acetylene-based glassy polymers and rubbery poly(dimethylsiloxane) (PDMS), a commercial membrane used for higher hydrocarbon/methane separation. PTMSP is the most permeable and most *n*-butane/methane selective polymer known. Poly(2-alkylacetylenes) follow the general permeability/selectivity relationship for *n*-butane/methane separation; that is, as *n*-butane permeability increases, a simultaneous increase in *n*-butane/methane selectivity is observed. However, linear poly(2-alkylacetylenes) show relatively poor performance compared to stiff-chain, high free volume, branched polyacetylenes, such as PTMSP, PMP, and disubstituted poly(diphenylacetylenes) or highly flexible, rubbery polymers, such as poly(dimethylsiloxane).

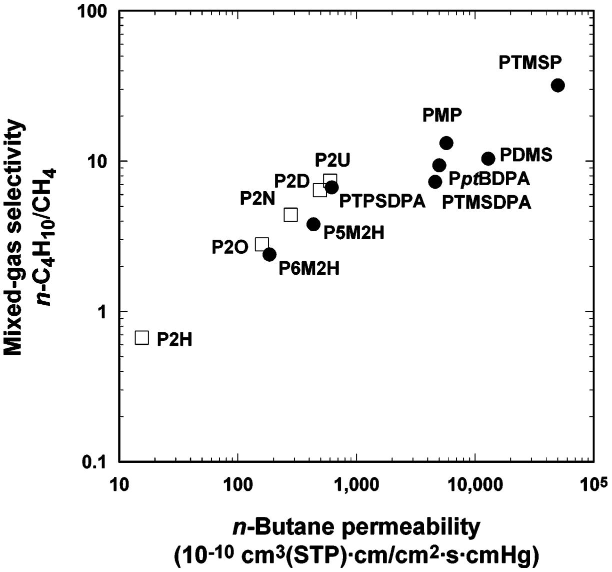

Figure 8. Relationship between mixed-gas *n*-butane permeability and *n*-butane/methane selectivity for a series of glassy polyacetylenes and rubbery poly(dimethylsiloxane) (PDMS). Feed pressure: 150 psig; permeate pressure: atmospheric (0 psig); temperature: 25 °C. PTMSP = poly(1-trimethylsilyl-1-propyne); PMP = poly(4-methyl-2-pentyne); P*pt*BDPA = poly(*p*-*tert*-butyldiphenylacetylene); PTMSDPA = poly[1-phenyl-2-[*p*-(trimethylsilyl)phenyl]acetylene]; PTPSDPA = poly[1-phenyl-2-[(*p*-triisopropylsilyl)phenyl]acetylene]; P5M2H = poly(5-methyl-2-hexyne); P6M2H = poly(6-methyl-2-heptyne); P2H = poly(2-hexyne); P2O = poly(2-octyne); P2N = poly(2-nonyne); P2D = poly(2-decyne); P2U = poly(2-undecyne).

Conclusions

The pure- and mixed-gas permeation properties were investigated for a systematic series of poly(2-alkylacetylenes). An increase in the length of the linear alkyl side chain leads to (i) lower fractional free volume, (ii) higher permeability, and (iii) higher mixed-gas *n*-butane/methane selectivity. Linear poly(2-alkylacetylenes) have relatively low fractional free volume (FFV 0.19−0.22), compared to polyacetylenes, containing bulky side substituents directly attached to the rigid −C═C− main chain, such as poly(4-methyl-2-pentyne) (FFV = 0.28) or PTMSP (FFV = 0.29). In poly(2-alkylacetylenes), the mixed-gas *n*-butane permeability and *n*-butane/methane selectivity increase with increasing side-chain length. This improvement in performance is caused by an increase in side-chain mobility as the side-chain length increases. However, compared to branched polyacetylenes, linear poly(2-alkylacetylenes) exhibit rather poor performance for *n*-butane/methane separation.

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