

Oxygen Permeation in SBS-g-VP Membrane and Effect of Facilitated Oxygen Carrier

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Synopsis

The grafting of 4-vinyl pyridine to styrene-butadiene-styrene triblock copolymer by radiation-induced graft copolymerization was studied. The membranes of various degrees of grafting were prepared by the solution casting method. The effect of grafting degree and operating temperature on membrane gas permeability were investigated. The effect of (*N,N'*-disalicylideneethylenediamine)cobalt (II) [CoS] on oxygen permeation through the SBS-g-VP membrane containing 10 wt % CoS was also studied.

INTRODUCTION

Membranes for gas separation have recently received much attention since membrane processes have the potential for energy efficient operation.¹ Essential requirements to such membranes are high permeability and high permselectivity for a particular gas. Kammermeyer² determined these properties for common gases such as O₂, N₂, H₂ and CO₂ in 1957. Michaels,³ in 1965, reported the permeation properties of natural rubber for a wide variety of gases and vapors. In 1965, Paul⁴ studied the separation of inert gas with poly(butadiene-co-styrene). When Robb,⁵ in 1967, reported the permeation properties of silicone rubber for a wide variety of gases and vapors, it was clear that rubber was a high permeable polymer for most gases but the permselectivity was low. Therefore much attention has been directed to modify rubber for gas separation processes.⁶⁻⁸

Metal complexes, such as cobalt Schiff base complex and iron porphyrin derivatives, form oxygen adducts reversibly and have been successfully used for an oxygen-transporting fluid⁹ and as an oxygen-separating liquid membrane.¹⁰ Recently there has been considerable interest in the production of oxygen-enriched air by the use of permselective membrane, which was prepared from a polymer complexed with the metal complex acting as a fixed carrier on oxygen permeation. In 1986, Nishide reported the preparation of polymer membranes containing the cobalt complexes as fixed carrier of oxygen which absorb and transport oxygen selectively by means of the Langmuir mode.¹¹ Drago and Balkus also reported that the cobalt-*N,N'*-bis[3-salicylidene-amino)propyl]methylamine complex bound to a polystyrene membrane enhances the selectivity for oxygen permeation through a polystyrene membrane

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at low pressures.¹² Sugie¹³ reported a new preparative method of a thin polymer-metal complex membrane, which showed high O₂/N₂ permselectivity.

This paper reports the preparation of styrene-butadiene-styrene-g-vinyl pyridine graft copolymer (SBS-g-VP) made by radiation-induced graft copolymerization. Then the membrane of SBS-g-VP prepared by solution casting method, and its performance of gas separation will be discussed. We also describe the selective and dual-mode transport of molecular oxygen in a polymer complexed with a cobalt-Schiff base as a fixed carrier. The polymer membrane was prepared by homogeneously complexing (*N,N'*-disalicylideneethylenediamine)cobalt(II) (CoS) to SBS-g-VP graft copolymer, whose sixth coordination site is vacant even in the solid state, to bind oxygen reversibly. Oxygen permeation is measured in connection with the upstream pressure. The oxygen-permeation behavior through the membrane will be discussed in terms of the dual mode transport theory.

EXPERIMENTAL

Materials

4-Vinyl pyridine was distilled under 5 mm Hg/54°C to eliminate impurities and was stored under nitrogen gas. Styrene-butadiene-styrene triblock copolymer (SBS) was Kraton 1101 of the Shell Company. The characteristics of Kraton 1101 are listed in Table I. SBS was dissolved in benzene, precipitated by methanol, and then dried in an oven. This procedure was repeated three times to make SBS free of antioxidant. Methanol and ethanol were dried with soda lime and then distilled. Benzene was extracted several times with 80 mL of concentrated sulfuric acid per liter of benzene, until it became colorless and was then distilled. Reagent grade chloroform was used without purification. (*N,N'*-disalicylideneethylenediamine)cobalt(II) (CoS) was synthesized as in the literature.¹⁴

Procedure for Graft Polymerization

Three grams of SBS particles were immersed in 4-vinyl pyridine-methanol (1/4, v/v) and 4-vinyl pyridine-ethanol-water (volume ratio = 1 : 2 : 2) solution. After standing for at least 48 h at 25°C, the solutions were purged with nitrogen for 10 min, and then irradiated at 25°C in a 3000 Ci Co⁶⁰ source with a dose

TABLE I
Molecular Characteristics of Kraton 1101

Total molecular weight	102 × 10 ³
Polystyrene (%)	30
Terminal PS block (<i>M_w</i>)	17 × 10 ³
Central PB block (<i>M_w</i>)	68 × 10 ³
Microstructure	
PB 1,4- <i>trans</i> (%)	42
PB 1,4- <i>cis</i> (%)	49
PB 1,2 (%)	9

rate of 0.231 Mrad/h. After irradiation, the particles were washed in an ultrasonic cleaner for 10 min, extracted with hot methanol for at least 48 h to remove homopolymer, dried in a vacuum oven, and weighed. The degree of grafting in weight percent was calculated by the equation

$$\% \text{ Graft} = \frac{W_f - W_i}{W_i} \times 100\%$$

where W_f and W_i are the final and initial weights of particles, respectively.

Film-Casting

1. SBS-g-VP with various degrees of grafting were dissolved in chloroform, then the solutions were poured onto a clean Teflon surface. After evaporation, a membrane with a smooth surface and known thickness was obtained. The film was then identified by IR spectra (Perkin-Elmer, Model 567).
2. The chloroform solution of SBS-g-VP and CoS was cast on mercury surface under the condition without oxygen and purging with nitrogen. This was followed by drying in vacuum, to yield a deep brown membrane with thickness of 100 μm and containing 10 wt % CoS.

Measurements of Stress-Strain Curve and Glass Transition Temperature

Membranes were cut in dimension of $30 \times 5 \times 0.15$ mm. Stress-strain curves were determined by Universal testing machine (Shimadzu DCS-500). The molecular weights between crosslinking point were determined by the following equation¹⁵

$$M_c = \frac{\rho RT}{\delta} (\alpha - \alpha^{-2})$$

where ρ = the density of the elastomer, T = the absolute temperature, δ = the tensile stress, $\alpha = L_f/L_o$, where L_o and L_f are the length of the specimen before and after stress is applied.

Measurement of Gas Permeability

The permeability coefficients were determined on a gas permeability apparatus (Yanaco, Model GTR-10) equipped with a detector. The principle of measurement is by evacuating the downstream side of the membrane to about 0.05 mm Hg, and providing the upstream side with air at various pressure for the test, the increase in the volume of a fixed downstream receiving container is determined. Permeation coefficient P is then calculated from the slope of the steady-state (where Fick's law holds) time-volume relationship.

RESULTS AND DISCUSSION

The Study of SBS-g-VP Graft Copolymer

As reported previously,¹⁶ polystyrene and poly(4-vinyl pyridine) have similar infrared spectra. However, styrene has five adjacent H atoms on the benzene ring; whereas the pyridine cycle of 4-vinyl pyridine has only two adjacent H atoms. The former has a peak of absorption at 700 cm^{-1} and the latter at 820 cm^{-1} . The spectrum of SBS-g-VP shows both peaks at 820 cm^{-1} and 700 cm^{-1} . Since the unreacted 4-vinyl pyridine and its homopolymer have been extracted with hot methanol, the SBS-g-VP was certainly a graft copolymer.

In Figure 1, the degree of grafting increases with total dosage, then levels off. As reported previously,¹⁷ the degree of grafting of irradiation-induced graft polymerization is affected by the molecular chain mobility; this is related to the solubility of molecules in the graft polymerization system. In the irradiation-induced graft polymerization, the viscosity of SBS-vinyl pyridine-methanol system is smaller than the viscosity of SBS-vinyl pyridine-ethanol-water system. Therefore, the active centers of propagation chain end in the grafted polymer chain branch can be easily determined, and the degree of grafting is smaller for SBS-vinyl pyridine-methanol system than that of SBS-vinyl pyridine-ethanol-water system.

As shown in Figure 2, the stress of SBS-g-VP was higher than that of SBS. According to previous study,¹⁸ the morphology of SBS-g-VP had mosaic pattern. The incompatibility between poly(4-vinyl pyridine) and polybutadiene caused microphase separation, which was performed as the physical permanent cross-linking point. And the grafting of 4-vinyl pyridine onto polybutadiene formed

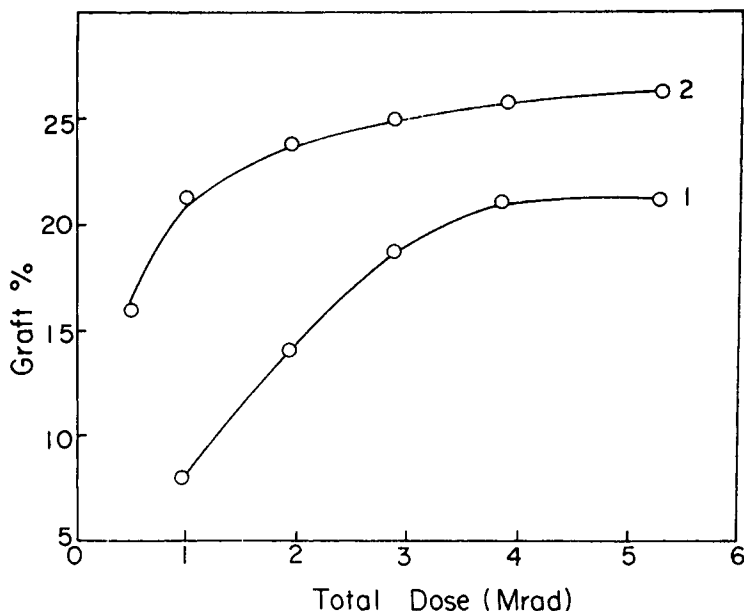


Fig. 1. Effect of radiation dose on grafting of vinyl pyridine to SBS with (1) methanol, (2) ethanol/H₂O as solvent.

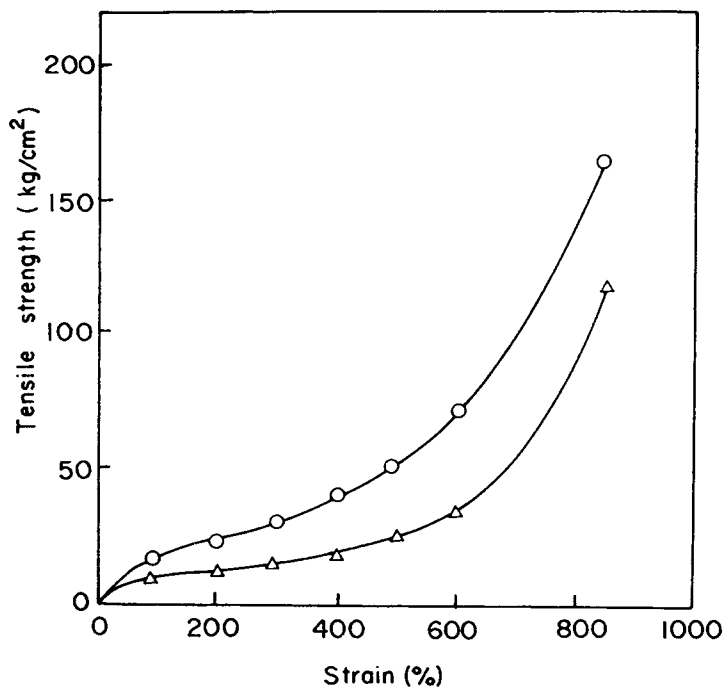


Fig. 2. Stress-strain curve of SBS-g-VP films: (○) 14% graft-on; (△) 0% graft-on.

a chemical crosslinking. So the stress of SBS-g-VP was higher than that of SBS. The glass transition temperature (T_g) and molecular weight between crosslinking point (M_c) are shown in Table II. T_g of SBS-g-VP was higher than that of SBS but M_c of SBS-g-VP was lower than that of SBS. And the existence of T_g at about -11°C for SBS-g-VP was resulted from the microphase separation between polybutadiene and polyvinyl pyridine. The results of Table II also confirmed the above discussion.

Effect of Grafting Degree and Operating Temperature on Membrane Gas Permeability

Figure 3 shows (1) the gas permeability decreased with the increasing degree of the grafting of 4-vinyl pyridine, (2) the O_2/N_2 selectivities of SBS-

TABLE II
Glass Transition Temperature (T_g) and Molecular Weight between Crosslinking Points (M_c) of SBS-g-VP

Degree of graft (%)	M_c^a	T_g^b ($^\circ\text{C}$)
0	2770	-94
14	1420	-90, -11

^a M_c are determined by the method of Ref. (15).

^b T_g is based on the polybutadiene block of SBS triblock copolymer.

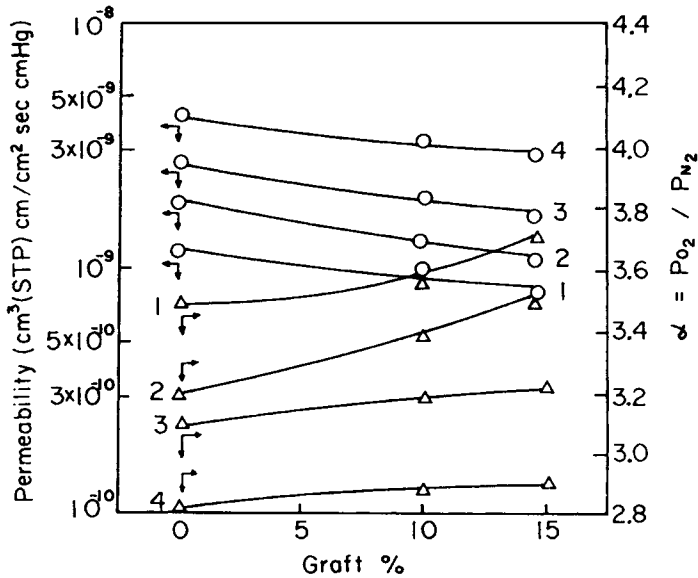


Fig. 3. Effect of grafting degree on permeability and selectivity at different temperature: (1) 273, (2) 283, (3) 293, (4) 303 K air operating pressure 113 cm Hg.

g-VP membrane were improved with the increasing degree of the grafting of 4-vinyl pyridine, and (3) the permeabilities of various degree of grafting SBS-g-VP membrane increased with increasing operating temperature in the temperature range of 273 to 303 K. However, the improvement was done at the expense of a decrease in O_2/N_2 selectivity. Comparing the results of 14% degree of grafting membrane to those of ungrafted membrane in Table III, the gas permeability decreased at various operating temperatures, (273, 283, 293, and 303 K). The decreasing ratios were 30%, 41%, 37.8%, and 28.8% for oxygen, and were 32.3%, 45.8%, 39.7%, and 31.3% for nitrogen. The decreasing ratio of nitrogen was higher than that of oxygen, so the O_2/N_2 selectivity increased.

When operating temperature was changed from 273 to 303 K, as shown in Table III, the gas permeability of nitrogen increased 341% for ungrafted membrane and 348% for 14% grafting degree membrane. The permeability of oxygen increased 250% and 256% for ungrafted and 14% grafting degree SBS-g-VP

TABLE III
Permeability and Selectivity of SBS-g-VP Membrane for O_2 and N_2

Graft %	Gas permeability			$P \times 10^{10}$			Separation factor			
	O_2			N_2			P_{O_2}/P_{N_2}			
	0	10	14	0	10	14	0	10	14	
Temperature (°C)	0	12	9.7	8.4	3.4	2.7	2.3	3.5	3.6	3.7
	10	19	13.0	11.2	5.9	3.8	3.2	3.2	3.4	3.5
	20	27	19.4	16.8	8.7	6.1	5.3	3.1	3.2	3.2
	30	42	33.5	29.9	15.0	11.5	10.3	2.8	2.9	2.9

membrane, respectively. It shows that the effect of operating temperature on gas permeability was larger for nitrogen than that of oxygen. The performance of grafted membrane was more affected by the operating temperature than that of ungrafted membrane.

The above behavior may be explained as follows: (1) From the values of solubility parameters, SBS is nonpolar polymer, [$\delta = 8.48$ (cal/cm³)^{1/2}], and vinyl pyridine is polar material ($\delta = 11$). When vinyl pyridine is grafted onto SBS, the higher is the degree of grafting, the larger is the value of solubility parameter. The difference between the solubility parameter of SBS-g-VP and oxygen, ($\delta = 4$), is large when the degree of grafting increased. Therefore the solubility of oxygen in SBS-g-VP membrane decreases with increasing degree of the grafting of 4-vinyl pyridine, and this is the same for nitrogen. (2) From the results of Figure 2 and Table II, it means that grafting of vinyl pyridine onto SBS increases the crosslinking density and enhances the polymer molecular chain interaction, so the chain mobility of SBS-g-VP is lower than that of SBS which will reduce the diffusivity of gas through SBS-g-VP. From the above discussion, the relative decreasing ratio of gas permeation for nitrogen is larger than that of oxygen and the O₂/N₂ selectivity increases. This is confirmed by the results in Table IV.

The activation energies (E_p) for gas permeation through SBS membrane as obtained by the Arrhenius law from Figure 4 are: 7.75 kcal/mol for nitrogen and 6.6 kcal/mol for oxygen. It shows that the energy barrier is higher for nitrogen through membrane than that of oxygen. So the effect of operating temperature on gas permeability of nitrogen is larger than that of oxygen. When the operating temperature increased, the gas permeability increased but the O₂/N₂ selectivity decreased.

Effect of Fixed Oxygen Carrier on Gas Permeability

Figure 5 shows that the upstream gas pressure (p_2) does not have any effect on the gas permeability of nitrogen and oxygen through SBS-g-VP membrane not containing CoS. And this is the same for nitrogen through SBS-g-VP membrane containing 10 wt % CoS. But the upstream gas pressure (p_2) has a pro-

TABLE IV
The Parameter of Gas Permeation through Membrane at 30°C, 113 cmHg Air Pressure

Membrane	Time lag, θ (s)		Diffusion coefficient ^a D (cm ² /s) $\times 10^6$		Solubility coefficient ^a S (cm ³ (STP)/ cm ³ -atm) $\times 10^2$	
	O ₂	N ₂	O ₂	N ₂	O ₂	N ₂
SBS	8	12	2.08	1.39	15.3	6.29
SBS-g-VP ^b	10	13	1.67	1.28	15.0	6.11
SBS-g-VP-CoS ^c	36	14	—	—	—	—

^a $D = l^2/6\theta$, $S = P/D$.

^b Graft percent = 10%.

^c CoS content = 10 wt %.

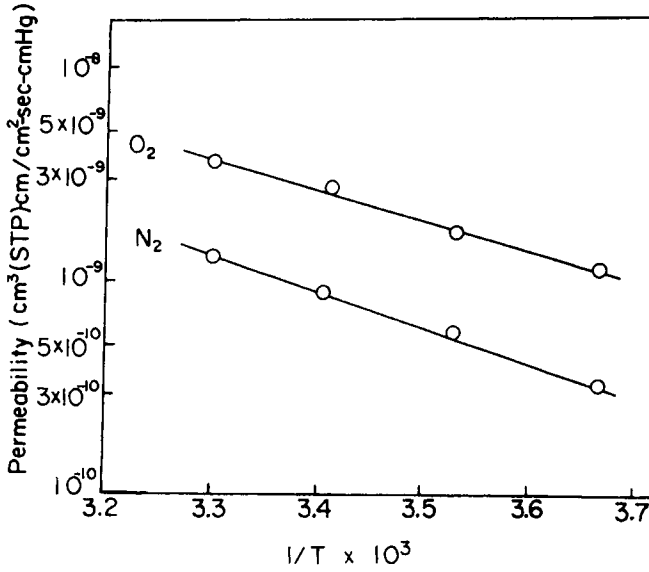


Fig. 4. Effect of operating temperature on gas permeability for SBS. Operating pressure was 113 cm Hg.

nounced effect on the gas permeation of oxygen through SBS-g-VP membrane containing 10 wt % CoS. In Table IV, the time lag of oxygen through SBS-g-VP membrane containing 10 wt % CoS is higher than that of SBS-g-VP membrane not containing 10 wt % CoS. But the time lag of nitrogen through SBS-g-VP membrane containing 10 wt % CoS is similar to that of SBS-g-VP mem-

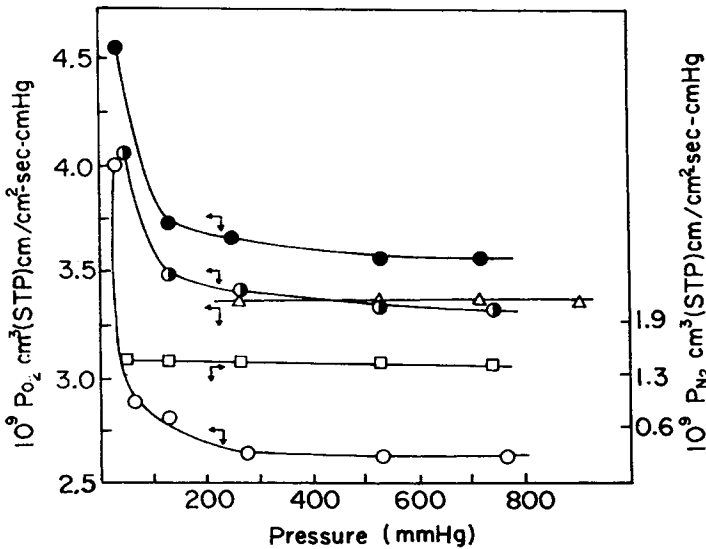
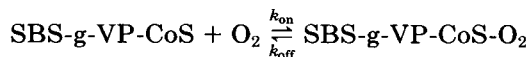


Fig. 5. Effect of upstream gas pressure on permeability for the SBS-g-VP/CoS membrane (oxygen at (\bullet) 40°C, (\bullet) 30°C, (\circ) 20°C; nitrogen at (\square) 30°C), and for SBS-g-VP membrane (oxygen at (Δ) 30°C).

brane not containing CoS. From the above results, it is clear that the existence of CoS has an pronounced effect on oxygen permeation but has little effect on nitrogen permeation. The phenomena are the same as observed in the studies of Tsuchida,¹¹ which were attributed to the reversible adsorption of oxygen on membrane containing CoS, as described below



where $\text{SBS-g-VP-CoS} = \text{SBS-g-VP}$ membrane containing CoS. k_{on} = the oxygen-binding rate constant of the CoS complexed to SBS-g-VP membrane and k_{off} = the oxygen-dissociation rate constant of the CoS complexed to SBS-g-VP membrane.

This is the Langmuir isotherm and suggests that oxygen permeation through SBS-g-VP membrane containing CoS occurs by means of a dual-mode transport mechanism (Henry mode and additive Langmuir mode).

From the study of ESR, the Co-O₂ adduct was observed even after pumping on the film under a vacuum. When the cobalt was nearly completely oxygenated, O₂ was not removed from the low pressure side of the film and the driving force for facilitated transfer of O₂ to the surface was removed. The O₂ adduct then inhibited the permeation through the film in comparison to the SBS-g-VP membrane without containing CoS by removing free volume. Therefore the permeability of O₂ for SBS-g-VP membrane without containing CoS was larger than that of SBS-g-VP membrane containing CoS, when the upstream gas pressure was larger than 400 mmHg.

Figure 5 shows that P increases with temperature. This may be due to the increase of gas moving-velocity and the easy dissociation of Co-O₂ adduct.

CONCLUSION

The degree of grafting initially increased with total irradiation dosage and then leveled off at 21% for SBS-VP-methanol system and at 26% for SBS-VP-ethanol-water system. The gas permeability of SBS-g-VP membrane decreased with increasing degree of grafting and the decrease of operating temperature. For example, comparing the gas permeability of 14% grafting degree SBS-g-VP membrane to those of ungrafted membrane at 283°K, the decreasing ratio were 41% for oxygen and 45.8% for nitrogen, respectively. When operating temperature was changed from 273°K to 303°K, the gas permeability of nitrogen increased 348% and that of oxygen increased 256% for 14% grafting degree SBS-g-VP membrane. The oxygen carrier, (N,N'-disalicylideneethylenediamine) cobalt (II), had a pronounced effect on oxygen permeation through SBS-g-VP membrane containing 10 wt % CoS that could be explained by dual-mode transport mechanism.

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References

1. For review, see: (a) H. K. Lonsdale, *J. Membr. Sci.*, **10**, 81 (1982); (b) W. Pusch and A. Walch, *Angew. Chem. Int. Ed. Eng.*, **21**, 660 (1982); (c) H. Strathmenn, *J. Membr. Sci.*, **9**, 121 (1981).

2. K. Kammermeyer, *Ind. Eng. Chem.*, **49**, 1685 (1957).
3. A. S. Michaels and H. J. Bixler, *J. Polym. Sci.*, **50**, 413 (1961).
4. D. R. Paul and A. T. DiBenedetto, *J. Polym. Sci.*, **C10**, 17 (1965).
5. W. L. Robb, *Ann. N.Y. Acad. Sci.*, **146**, 119 (1967).
6. W. J. Ward III, W. R. Browall, and R. M. Salemme, *J. Membr. Sci.*, **1**, 99 (1976).
7. M. Kawakami, Y. Yamashita, M. Iwamoto, and S. Kagawa, *J. Membr. Sci.*, **19**, 249 (1984).
8. D. H. Springmann, *Chem. Econ. Eng. Rev.*, **14**, 17 (1982).
9. (a) E. Tsuchida, *J. Macromol. Sci., Chem.*, **A13**, 545 (1979); (b) E. Tsuchida, H. Nishide, M. Yuasa, E. Hasegawa, Y. Matsushita, and K. Eshima, *J. Chem. Soc., Dalton Trans.*, 275 (1985). (c) E. Tsuchida, *Ann. N.Y. Acad. Sci.*, **446**, 429 (1985). (d) E. Tsuchida, *Chem. Eng. New*, **14**, 42 (1985).
10. I. C. Roman and I. W. Baker, Eur. Patent 98731 (1983).
11. (a) H. Nishide, M. Ohyanagi, O. Okada, and E. Tsuchida, *Macromolecules*, **19**, 494 (1986); (b) H. Nishide, M. Ohyanagi, O. Okada, and E. Tsuchida, *Macromolecules*, **20**, 417 (1987).
12. R. S. Drago and K. J. Balkus, *J. Inorg. Chem.*, **25**, 716 (1986).
13. K. Sugia, *Am. Chem. Soc. Polym. Mater. Sci. Eng.*, **59**, 139 (1988).
14. R. H. Bailes and M. Calvin, *J. Am. Chem. Soc.*, **69**, 1896 (1947).
15. L. R. G. Treloar, *The Physics of Rubber Elasticity*, Oxford University Press, London (1958).
16. J. M. Yang and G. H. Hsiue, *Angew. Makromol. Chem.*, to appear.
17. J. M. Yang and G. H. Hsiue, *J. Appl. Polym. Sci.*, to appear.
18. G. H. Hsiue and Z. K. Yeh, *Angew. Makromol. Chem.*, **153**, 33 (1987).

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