Chemistry Faculty Research & Creative Works   Chemistry

10 Aug 1984

Preparation Of Gas Separation Membranes By Plasma Polymerization With Fluoro Compounds

H. Nomura

P. W. Kramer

H. Yasuda
Missouri University of Science and Technology, yasudah@mizzou.edu

Recommended Citation

PREPARATION OF GAS SEPARATION MEMBRANES BY PLASMA POLYMERIZATION WITH FLUORO COMPOUNDS*

H. NOMURA, P. W. KRAMER AND H. YASUDA

Department of Chemical Engineering and Graduate Center for Materials Research, University of Missouri-Rolla, Rolla, MO 65401 (U.S.A.)

Plasma polymerization coatings were applied for the preparation of gas separation membranes. Mainly fluoro compounds were used as coating materials. The membranes showed good separation characteristics with high flux for gaseous systems. The plasma polymerization composite parameter given by W/FM plays an important role in obtaining excellent separation characteristics. The correlation between the conversion rate DR/FM, where DR is the deposition rate of plasma polymer, and W/FM is useful to consider the plasma polymer character under the different plasma polymerization conditions (discharge power W and monomer flow rate F). The proper conditions for membrane preparation lie in the intermediate region between the region in which the monomer flow rate is deficient and that in which the discharge power is deficient. Furthermore, the plasma polymerization coatings with the higher molecular weight monomer gave the higher separation characteristics. Plasma polymer composite membranes in this study showed superiority for the molecular sieve type of separation over the solution–diffusion type of separation.

1. INTRODUCTION

The application of plasma polymerization coating to prepare membranes for use in gas separation is a completely different concept compared with conventional membrane preparation. In the conventional method of preparing the membrane, efforts are made to make the effective membrane layer thinner[1]. In many cases, films which are formed by plasma polymerization are deposited in networks of highly branched and highly cross-linked segments. Also, the interaction of the plasma polymer with the substrate and the unique mechanism of polymer formation give excellent adhesion of a thin deposit to the substrate. This technique solves many problems associated with conventional methods of membrane preparation. The application of plasma-polymerized films as membranes has been the subject of much research effort. The main area of this research has been the use of such membranes in

---

the reverse osmosis desalination of sea water or brackish water[2-4]. In the area of gas separation membranes prepared by plasma polymerization very few studies have been reported. Stancell and Spencer[5] reported on the improvement in permselectivity for the H_2–CH_4 system by using plasma-polymerized thin films deposited onto relatively permeable substrates.

In this study plasma-polymerized coatings from fluoro compounds were applied to porous polysulfone hollow fibers to prepare membranes to be used for the separation of several binary gas mixtures. The effects of the conditions used during the plasma polymerization process on the membrane performances are discussed.

2. EXPERIMENTAL DETAILS

2.1. Plasma reactor system

The reactor system used in this study is shown in Fig. 1(a). It consists of two glass reaction vessels in series, each containing a pair of circular stainless steel electrodes. The fibers are stored on six spools at the bottom of the reactor system. The fibers are drawn upwards between the electrodes by a motor-driven take-up spool at the top of the equipment.

An MKS Baratron type 170 pressure meter is connected to each reaction chamber for determining the flow rate of the monomer vapor and monitoring the pressure during the glow discharge. These instruments are capable of measuring a vacuum in the range of 10^{-5}–1 Torr independent of the gas nature or composition.

The plasma reactor can be operated over a range of frequencies from low frequency a.c. to r.f. However, in this study, an audio frequency of 10 kHz was applied.
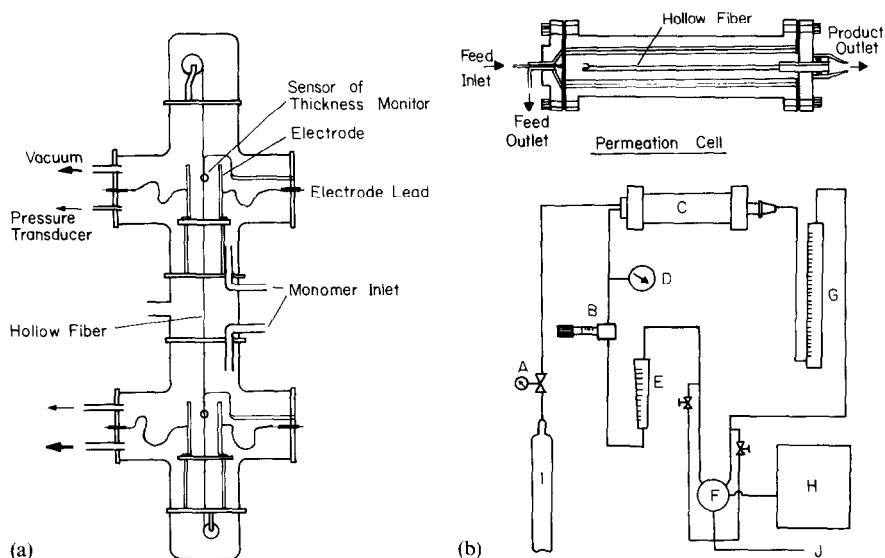

Fig. 1. Schematic diagrams of (a) the plasma reactor system and (b) the test apparatus for gas separation (A, pressure regulator; B, needle valve; C, permeation cell; D, pressure gauge; E, flowmeter; F, sample selector; G, bubble flowmeter; H, gas chromatograph; I, gas cylinder; J, waste).

The sensor of a thickness monitor (crystal sensor, IPN-007-210; monitor, model XTM, Inficon) is located in the interelectrode space. Deposition rates of polymerization were measured at 20 °C. Coating thickness was estimated from the values of the deposition rate (in ångströms per second) and the fiber residence time (in seconds) in the plasma region.

2.2. Membrane preparation

Hollow fiber units were prepared according to the following procedure.

2.2.1. Plasma polymerization coating

Liquid monomers are fed to the reactor by evaporation from a small glass bulb. The monomer flow rate to the plasma reactor is set by means of a needle valve. Gas monomers are fed by means of a flow controller (Tylan mass flow controller model 260; readout box, R0-20A).

To pull the hollow fibers through the reactor system, the controller of the d.c. motor is set to the estimated dial setting corresponding to the desired pulling speed.

The glow discharge was carried out by adjusting the current and voltage to maintain a preselected wattage.

2.2.2. Fiber potting

Hollow fibers must be "potted" prior to the gas separation experiment. The fibers are held in place inside a stainless steel tube by a rubber stopper and hardened resin (Shell Epon resin 215; curing agent, Magnolia 235).

2.3. Gas separation

The apparatus used for gas separation is shown in Fig. 1(b). The cell was a stainless steel pressure chamber consisting of three detachable parts. The hollow fiber unit was set in the right-hand part of the cell as shown in Fig. 1(b). The gas which permeated the membrane was withdrawn at atmospheric pressure.

The experiments were carried out at laboratory temperature. The applied gauge pressure was $100 \, \text{lbf in}^{-2}$.

In order to reduce the concentration polarization near the membrane surface, the flow rate of feed gas was kept by the needle valve in the range $0.2-0.7 \, \text{l min}^{-1}$ (the flow rate of feed gas was about 100 times greater than the permeation rate). The flux was measured by means of a bubble flowmeter.

The flux $J \, (\text{m}^3 \, \text{m}^{-2} \, \text{s}^{-1})$ through a membrane is generally expressed as

$$J = P \frac{\Delta p}{l}$$

where $P \, (\text{m}^3$ (standard temperature and pressure) $\text{m} \, \text{m}^{-2} \, \text{s}^{-1} \, \text{atm}^{-1})$ is the permeability coefficient and Δp (atm) is the pressure difference across a membrane of thickness l (m). For a composite membrane, the gas flux constant P/l is suitable to express the permeability of gases since the permeability coefficients of the coating layer and the substrate cannot be determined separately. In the case of a hollow fiber, the membrane area is properly calculated using the logarithmic mean of the inside and outside diameters.

The enrichment factor β is defined as

$$\beta \left(\frac{X_A}{X_B}, \Delta p \right) = \frac{Y_A}{X_A}$$

$$\beta\left(\frac{X_B}{X_A}, \Delta p\right) = \frac{Y_B}{X_B}$$

where X_A and X_B are mole fractions in the feed and Y_A and Y_B are those in the product for components A and B respectively when the operation pressure difference is Δp.

The separation factor γ is also used:

$$\gamma\left(\frac{X_A}{X_B}, \Delta p\right) = \frac{Y_A/Y_B}{X_A/X_B} = \frac{Y_A/X_A}{Y_B/X_B} = \frac{\beta(X_A/X_B, \Delta p)}{\beta(X_B/X_A, \Delta p)}$$

In this study, compressed air ($X_{O_2}/X_{N_2} = 21/79$) was used for the feed, and the component ratios of the other gas mixtures, *i.e.* H_2–N_2, H_2–CO_2, He–CH_4 and CO_2–CH_4, were $X_A/X_B = 50/50$.

The concentrations of components were determined by means of gas chromatography (gas chromatograph GC-6AM, Shimadzu Co., Japan). A data processor (Chromatopac C-R1B, Shimadzu Co., Japan) was used for monitoring and calculating the gas composition in the feed side and the product side.

3. RESULTS AND DISCUSSION

3.1. Conditions of plasma polymerization coating

The membranes used are composite membranes which were prepared using plasma polymerization coating. In the plasma polymerization coating, the discharge power and monomer flow rate are important factors since these two factors control the deposition rate of plasma polymerization and the characteristics of the coating layer.

Generally, plasma polymerization can be divided into three regions: (1) the power-deficient region, (2) the region in which the monomer flow rate is deficient and (3) the region which is intermediate between (1) and (2). To define the above regions clearly, the composite factor W/FM, which consists of the discharge power W, the monomer flow rate F and the molecular weight M is useful, since W or F cannot be discussed as independent variables in plasma polymerization[6]. Furthermore, this parameter represents the amount of energy supplied per unit mass of the monomer. The correlation between the conversion factor DR/FM, where DR is the deposition rate of plasma polymer, and the parameter W/FM is useful in considering plasma polymerization characteristics and the characteristics of the deposited polymer. The above treatment for plasma polymerization results is shown in Fig. 2 for perfluoro-2-butyltetrahydrofuran. In spite of different discharge power and monomer flow rates, the correlation between the conversion factor DR/FM and the composite factor W/FM showed one trend from the lower W/FM region to the higher W/FM region. In particular, the relation was linear in the lower W/FM region which is the power-deficient region.

3.2. The effect of W/FM on the enrichment factor $\beta(X_{O_2}/X_{N_2} = 21/79$; $\Delta p = 6.8$ atm)

The effect of W/FM on the enrichment factor $\beta(X_{O_2}/X_{N_2})$ for the separation of

a compressed air mixture was examined using plasma-polymerized perfluoro-2-butyltetrahydrofuran coatings. The results are shown in Fig. 2, which also shows the effects of coating thickness at the various W/FM values. In general, the enrichment factor $\beta(X_{O_2}/X_{N_2})$ increased with increasing coating thickness. The decrease in $\beta(X_{O_2}/X_{N_2})$ at a coating thickness of 2500 Å for the films prepared at a W/FM value of 4.92×10^7 J kg^{-1} could be due to cracking of the coated film, but why this film showed this behaviour and the others did not is still being investigated. Figure 2 also shows that the enrichment factor increases with increasing W/FM up to a W/FM value of 1.29×10^8 J kg^{-1} and then decreases sharply with increasing W/FM.

In order to explain the above observations, one scheme was considered as shown in Fig. 3. The internal tension in the polymer network depending on the composite factor W/FM governs the coating characteristics (non-effective coating,
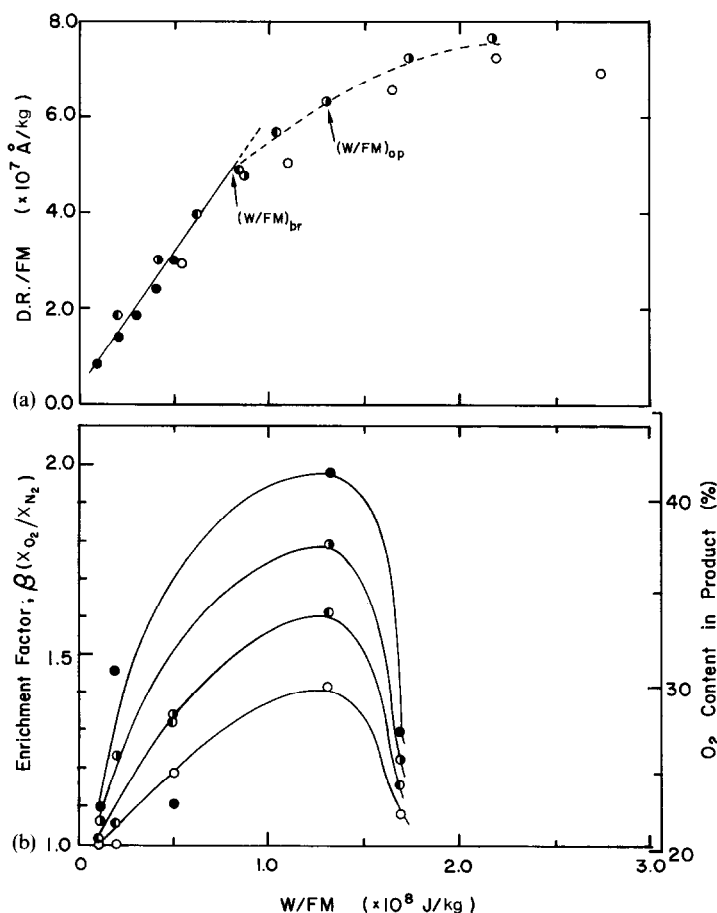

Fig. 2. (a) Correlation between the conversion factor DR/FM and the parameter W/FM for various monomer flow rates (in cubic centimeters at standard temperature and pressure per minute): ○, 0.59; ◐, 0.75; ◑, 1.56; ●, 3.11. (b) Effect of the parameter W/FM on the enrichment factor $\beta(X_{O_2}/X_{N_2}) = 21/79$; $\Delta p = 6.8$ atm) at various coating thicknesses (in ångströms): ●, 2500; ◐, 2000; ◑, 1500; ○, 1000.

effective coating, coating with cracks). The non-effective coating region results from two different effects: (1) the coating is not thick enough to cover completely all the pores in the substrate and (2) there is insufficient internal stress within the polymer network of the coating to have any effect on the separation characteristics of the membrane. An effective coating, one which increases the permselectivity of the membrane, is one which falls in the region between the two curves in Fig. 3.
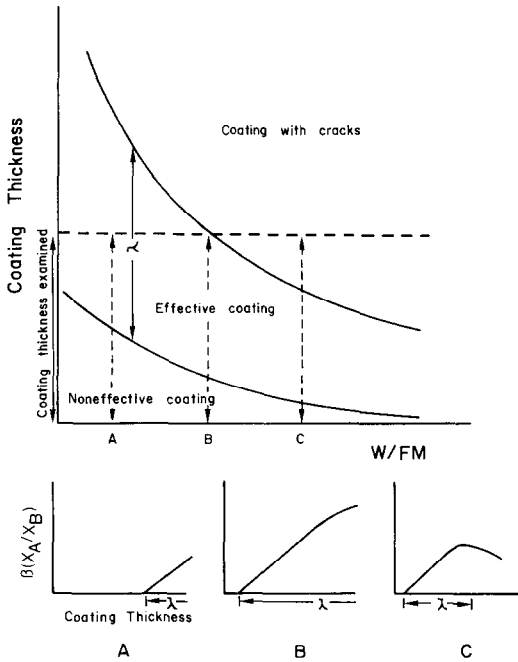

Fig. 3. Schematic representation of the characteristics of plasma coating (λ, effective thickness range in which a plasma polymer offers effective coating).

When the internal stress within the coating becomes too great, cracks occur in the coating. This cracking occurs at the greater thicknesses and detrimentally affects the separation characteristics of the composite membrane. Figures 3A–3C show the effects of the above interpretation on the membrane performance, namely the enrichment factor $\beta(X_A/X_B)$. In case A a large coating thickness is necessary before any improvement in the enrichment factor can occur, because of the weak internal stress within the plasma polymer network at low thicknesses. Case B shows the best behavior of the three since the effect of low internal tension is small and the range of coating thicknesses which are effective is fairly broad. In case C the non-effective coating region is small but the increase in internal tension with increasing coating thickness is fairly rapid so that cracks occur in the coating at relatively low thicknesses.

3.3. Optimum conditions for membrane preparation

The effect of W/FM on membrane performances was clearly seen in the variation in the enrichment factor $\beta(X_{O_2}/X_{N_2})$ shown in Fig. 2. In order to determine

which conditions should be applied during the plasma polymerization process, the relationship between the conversion factor DR/FM and W/FM was found to be very useful. For a monomer which shows a breaking point $(W/FM)_{br}$ in the relationship between DR/FM and W/FM it was fairly easy to determine an optimum value of W/FM at which the enrichment factor was maximized. The breaking point W/FM is that value of W/FM at which the relationship between DR/FM and W/FM begins to deviate from the initial linear relationship. For the monomers investigated in this study, those which showed a maximum in the enrichment factor *versus* W/FM relationship had this maximum at a W/FM value which was in the intermediate region of the DR/FM *versus* W/FM curve, *i.e.* between the power-deficient and monomer-deficient regions. Table I shows this for the perfluorocarbons, namely that $(W/FM)_{op}$ is slightly higher than $(W/FM)_{br}$. In the cases of silicon tetrafluoride and pentafluorostyrene, no breaking point was observed in the DR/FM *versus* W/FM relationship and the separation characteristics were poor for all the membranes, no matter what plasma polymerization conditions were applied during the membrane coating. Table I also contains a listing of the specific bonding energies for each of the monomers. The specific bonding energy was calculated as the total bonding energy divided by the molecular weight of the monomer. The values of $(W/FM)_{br}$ for the perfluorocarbons are three to four times the specific bonding energies. Propylene shows a break point at about five times the specific bonding energy but the optimum W/FM is similar to that of the perfluorocarbons. This difference can be attributed to the difference between hydrocarbons and fluorocarbons in the plasma polymerization process; however, further studies are necessary to substantiate this observation.

3.4. Selection of monomer for plasma polymerization coating

The relationship between the separation factor $\gamma(X_A/X_B)$ and the molecular weight of the starting monomer used for the plasma polymerization coating is shown in Fig. 4. The five binary gas systems are divided into two groups. The separations

TABLE I

OPTIMUM W/FM FOR MEMBRANE PREPARATION RELATED TO SPECIFIC BONDING ENERGY

Monomer	Series	Specific bonding energy $\Sigma E_b/M$ [a] ($J\,kg^{-1}$)	Breaking point W/FM value $(W/FM)_{br}$ [b] ($J\,kg^{-1}$)	Optimum W/FM value $(W/FM)_{op}$ [c] ($J\,kg^{-1}$)
Perfluoro-2-butyl-tetrahydrofuran	110	2.60×10^7	8.2×10^7	12.9×10^7
Propylene	140	8.20	42.0	11.4
Hexafluoropropylene	150	2.57	10.0	6.61
Silicon tetrafluoride	160	2.36	—	—
Pentafluorostyrene	170	3.94	—	—
Perfluoro-1-methyldecaline	180	2.60	8.0	9.3

[a] $\Sigma E_b/M$, total bonding energy divided by molecular weight.

[b] $(W/FM)_{br}$, estimated in the relation between the conversion factor DR/FM and W/FM.

[c] $(W/FM)_{op}$, observed W/FM value for which the best membrane performances were obtained in the series of membranes.

for the gas systems shown in Fig. 4(a) are dependent mainly on the difference in molecular size of the gas molecules, *i.e.* the smaller size gas permeates faster; this type of separation is called molecular sieve separation. The separation of the gas systems shown in Fig. 4(b) is dependent on solution–diffusion permeation, *i.e.* the larger gas permeates faster because of its higher solubility in the membrane polymer.

The plasma polymerization coatings prepared from the higher molecular weight monomer gave the higher separation characteristics for both types of separation; however, the separation factors obtained with the plasma polymers are similar to or smaller than typical separation factors for conventional polymers.

The results shown in Fig. 4(a) for the H_2–CO_2 system show the effects the solubility of the penetrating molecule has on the separation characteristics of a membrane: not much variation is observed in the value of the $\gamma(X_{H_2}/X_{CO_2})$ which is low (close to unity). This is because, even though the H_2 molecule is small and can permeate through the membrane easily, the high solubility of CO_2 in the membrane allows it to permeate at a similar rate.

The apparently anomalous behavior for membranes prepared by plasma polymerization of pentafluorostyrene can be attributed to the fact that the correlation between DR/FM and W/FM for this monomer did not show a breaking point within the range of W/FM values obtainable in this study. For this reason all the conditions applied during the membrane preparation fell in the power-deficient region. Membranes prepared from other monomers using conditions which fell in the power-deficient region yielded poor membranes.

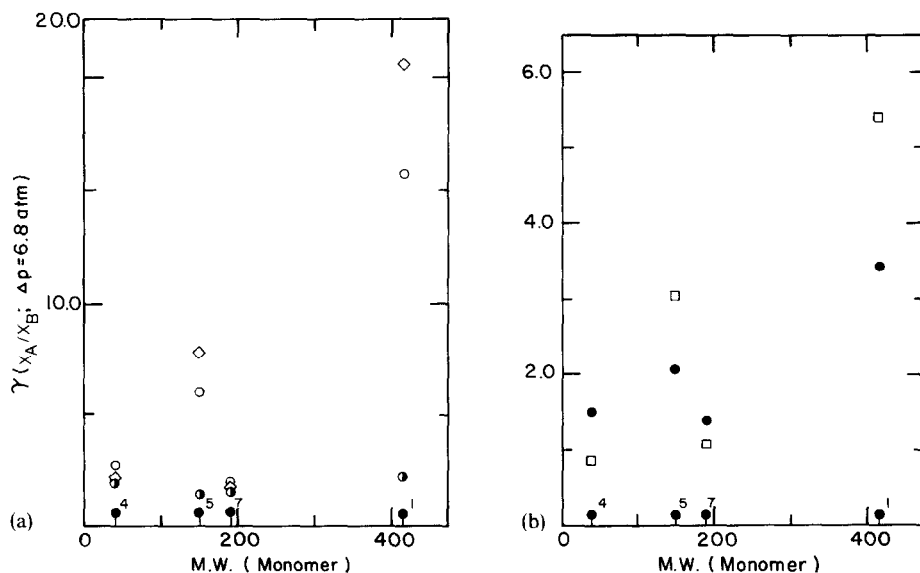The effect of the molecular weight of the starting monomer on the separation

Fig. 4. Effect of molecular weight of starting monomer (1, perfluoro-2-butyltetrahydrofuran; 4, propylene; 5, hexafluoropropylene; 7, pentafluorostyrene) on the separation factor $\gamma(X_A/X_B)$; $\Delta p = 6.8$ atm): (a) molecular sieve type of separation for the gas mixtures 50%H_2–50%N_2 (○), 50%H_2–50%CO_2 (◑) and 50%He–50%CO_2 (◇); (b) solution–diffusion type of separation for the gas mixtures 21%O_2–79%N_2 (●) and 50%CO_2–50%CH_4 (□).

characteristics is more marked for the molecular sieve type of separation than for the solution–diffusion type of separation, as can be seen by noting the magnitudes of $\gamma(X_A/X_B)$ in both figures.

4. CONCLUSIONS

The plasma polymerization composite factor W/FM plays an important role in obtaining composite membranes with good separation characteristics. The relationship between the conversion factor DR/FM and W/FM is very useful in determining which conditions (monomer flow rate, discharge power) to apply during the plasma polymerization process to obtain an effective coating. In particular, for the perfluorocarbons investigated in this work, the maximum enrichment factor was obtained for membranes which had been coated at plasma polymerization conditions which fell in the region between the power-deficient and monomer-deficient regions.

Furthermore, the effect of the molecular weight of the starting monomer on the membrane performances is remarkable in the series of fluorocarbons investigated. This effect is greater for the molecular sieve type of separations than for the solution–diffusion type of separations. The plasma-polymerized coatings from higher molecular weight monomer gave higher separation characteristics.

REFERENCES

1 W. L. Robb, *General Electric Rep. 65-C-031*, 1965.
2 H. Yasuda and C. E. Lamaze, *J. Appl. Polym. Sci.*, *17* (1973) 201.
3 A. T. Bell, T. Wydeven and C. C. Johnson, *J. Appl. Polym. Sci.*, *19* (1975) 1911.
4 H. Yasuda, Composite reverse osmosis membranes prepared by plasma polymerization. In S. Sourirajan (ed.), *Reverse Osmosis Synthetic Membranes*, National Research Council of Canada, Ottawa, 1977, pp. 263–294.
5 A. F. Stancell and A. T. Spencer, *J. Appl. Polym. Sci.*, *16* (1972) 1505.
6 H. Yasuda and T. Hirotsu, *J. Polym. Sci., Polym. Chem. Edn.*, *16* (1978) 743.