Preparation, Characterization, and Permeation Property of a Liquid Crystal/PDMS Membrane Material

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ABSTRACT: By introducing the ordered and flowing liquid crystalline groups into polymeric membranes, a novel liquid crystal/polydimethylsiloxane (LC/PDMS) membrane material is synthesized with PDMS containing vinyl group, polymethylhydrosiloxane and cholesteric LC as matrix materials. The chemical structure, LC behaviors and mechanical performance of the LC/PDMS crosslinked membranes are characterized by using FTIR, differential scanning calorimetry (DSC), and polarized light microscopy with a hot stage. Some factors on permeability and permselectivity for carbon dioxide and nitrogen gas are also examined. These results suggest that the membrane-forming property and permeation properties of the crosslinked membranes are obviously enhanced due to the introduction of the LC groups into PDMS and crosslinking reaction in the preparation process. At pressure difference of 0.1 MPa and testing temperature of 40°C, the permeability coefficient for carbon dioxide and ideal separation factor for carbon dioxide and nitrogen are up to 4667 Barrer and 24.0, respectively. In addition, the incorporation of LC containing unsaturated linkage has the potential for further modification reactions such as grafting and crosslinking. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 191–199, 2012

Key words: liquid crystals; polymeric membrane; membrane materials; gas separation

INTRODUCTION

Global warming has been identified as one of the world's major environmental issues.[1] While it is impossible to completely stop the effects of anthropological global warming, it is possible to mitigate carbon dioxide gas which has key effect on global warming. Therefore, new methods of removing carbon dioxide from natural gas must be devised. While capture of carbon dioxide with amine solvents is the most mature technology, another possible contender is gas separation membranes. Among all polymers currently available applied to separate CO_2, attentions have been focused primarily on glassy section or block of the polymers in the scientific literature recently. Examples of polymers used in the construction of gas separation membranes include polyacetylene, polyarylate, polycarbonate, polyetherimide, poly(ethylene oxide), polyimide, and poly(phenylene oxide), etc.[2–7]

Polydimethylsiloxane (PDMS) has been long utilized industrially as a special membrane material for the separation of gas mixtures due to its very high permeation rate.[2,8] However, the selectivity of this membrane for a particular gas mixture is very low. To improve its selectivity value without drastically reducing its permeation rate, lots of literatures based on the chemical structure modifications are available. And attempts have been made to improve permeability property of PDMS by modifying backbone and side-chain of PDMS or mixing with other polymers.[9–11] For these purposes, different functional groups have been introduced into the backbone or side chains of PDMS to improve the intrinsic selectivity, which is usually accompanied by general decrease in permeability.[12,13] Hence, functionalization of polymeric membrane is important for enhancing surface interactions with specific chemicals to enhance separation.[14] Crosslinked is a simple and effective way to change the structure of PDMS membrane and to improve selectivity. Crosslinked methods include covalent bond and metal ion bond crosslinked, from which an ionomer can be formed.[15] In addition, crosslinked also offer the potential to improve the mechanical and thermal properties of polymeric membrane. Koros has suggested that crosslinked can be used to increase membrane stability in the presence of aggressive feed gases and to simultaneously reduce plasticization of the membrane.[16] Unnikrishnan has investigated the

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effect of the nature of crosslinked on the diffusion and transport of aromatic hydrocarbons through natural rubber membranes.[17]

Much of the research work is being devoted to the development of membranes that exhibit both a higher selectivity and a higher intrinsic permeability to specific gases than the membranes available at present. Nowadays, liquid crystal membrane (LC) has received considerable attention as a special membrane material for gas separation due to its soft and ordered structure.[18,19] By imitating the surficial structure and shape of biological membranes, LC membranes present an interesting approach to improving the gas separation properties by introducing the ordered and flowing LC into the polymeric membranes. Li prepared triheptyl cellulose/ethyl cellulose binary blend membranes from tetrahydrofuran, chloroform and dichloromethane solutions and studied their oxygen enrichments at different temperatures and operating times.[20] However, under external environment influence, the LC composite might separate from the above polymer/LC composite membranes, resulting in a decreasing of permeability or selectivity. If the LC composite is covalently introduced into the side-chains of PDMS by crosslinked method, the membrane-forming ability and permeation property of the modified PDMS membrane may be improved obviously. Of course, the modified method cannot only avoid transferring and removing of the LC composite, but also improve biocompatibility of polymeric materials.

To overcome these disadvantages of PDMS membranes and LC membranes at present, in the article we selected PDMS containing vinyl groups and cholesterolic LC containing unsaturated linkage as matrix materials, and polymethylhydrosiloxane as a crosslinked agent, a chloroplatinic acid solution as a catalyst. A novel LC/PDMS membrane material was prepared by silicone-hydrogen addition reaction. The objective of the present work is to discuss several factors on permeability and permselectivity for the crosslinked membranes.

EXPERIMENTAL

Materials

Polydimethylsiloxane (PDMS), polymethylhydrosiloxane and a chloroplatinic acid solution (as a catalyst) were purchased from the Research Center of Organic Silicone of Chengdu, China. The number-average molecular weight of silicone rubber was 500,000, and the vinyl content was 10% (molar percentage). The hydrogen content of polymethylhydrosiloxane was 1.5% (mass percentage). Vinylacetic acid cholesterol ester, 4-pentenoic acid cholesterol ester, 3-hexenoic acid cholesterol ester and 11-alkenoic acid cholesterol ester were obtained from Alfa Aesar. All other solvents and chemical agents were analytical grade and used without further purification. Pure gases, CO_2 and N_2, were purchased from Guangzhou Gas, China. All the gases used had a minimum purity of 99.9%.

Instruments and measurements

Mechanical properties of these membrane materials were measured by Shimadzu AG-I of Japan. Every sample was tested three times under room temperature. Infrared measurements were obtained with Bruker EQUINX 55 of German. LC behaviors of the cholesterol esters were characterized by using polarized microscopy with a hot stage (XPT-7, produced by Nanjing Optical Instrument). Differential scanning calorimetry (DSC) was conducted with Perkin–Elmer DSC-2C thermal analyzer at a heating rate of 10°C/min under a nitrogen atmosphere.

Membrane preparation

Cholesterol ester LC (0.25 g) and PDMS containing vinyl groups (1.0 g) were dissolved in 25 mL THF to form a solution. Subsequently, polymethylhydrosiloxane (0.012 g) and proper chloroplatinic acid solutions were added slowly into the solution. The crosslinking reaction continued for different times (such as 5, 10, 15, 20, and 25 min) at room temperature. Finally, the LC/PDMS crosslinked membranes were obtained by casting the sol onto a polyethylene terephthalate (PET) sheet at room temperature. These membranes were dried in an oven for 1 h at 60°C in the presence of air. The resulting membranes were easily removed and dried under vacuum for 24 h to remove any residual solvent. The membranes were $\sim$ 30 μm thick, roughly calculated by determining the thickness of more than five locations on any membranes.

Permeation measurement

The carbon dioxide and nitrogen permeability coefficients (1 Barrer $= 10^{-10}$ cm^3 (STP) cm/(cm^2 s cmHg)) of the membranes were measured according to the variable-volume method of Stern.[21] The operation process are described elsewhere.[22,23] The permeability coefficient for carbon dioxide (P_{CO_2}) and nitrogen permeability coefficient (P_{N_2}) and ideal separation factor ($\alpha CO_2/N_2$) were calculated using the following equations[24]:

$$P = \frac{\Delta V \cdot l}{A \cdot \Delta p \cdot \Delta t} \tag{1}$$

$$\alpha_{CO_2/N_2} = \frac{P_{CO_2}}{P_{N_2}} \tag{2}$$

where ΔV and Δt were the changes in volume for the permeated gas and in time, respectively; A and l

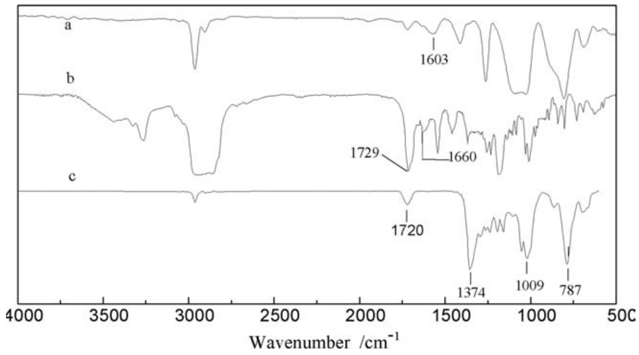


Figure 1 FTIR spectra of PDMS (a), cholesterol ester liquid crystal (b), and the crosslinked membrane (c).

were the effective area and thickness of the membrane, respectively; Δp was the gas pressure difference across the membrane. The measurement conditions included that testing temperatures changed from 20 to 50°C and gas pressure differences across the membranes varied from 0.05 MPa to 0.4 MPa. And A was 3.8 cm^2. Each value of Δt was obtained by determining at least three times. The standard deviation was within ca. ±5%. Pressure was usually corrected to standard conditions (STP) of temperature (273°C) and pressure (76 cmHg). The assembled apparatus was immersed in a constant temperature bath, whose temperature could be controlled to within ± 0.1°C by means of a mercury thermoregulator. The apparatus and experimental procedure employed for the gas permeability measurements had been described in the previous literatures.[24,25]

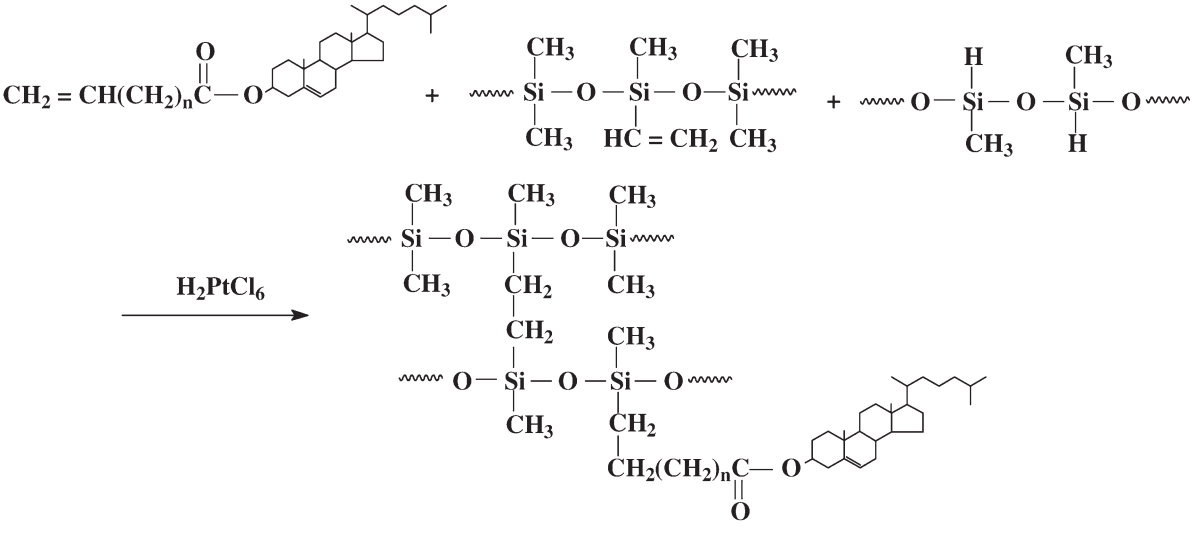
RESULTS AND DISCUSSION

Synthesis and characterization

The chemical structure changes during the crosslinking process were monitored by fourier transform infrared spectroscopy (FTIR) and shown in Figure 1. By controlling the molar ratio of PDMS, cholesteric LC and polymethylhydrosiloxane, each molecular units containing two hydrogen atoms for the crosslinked agent can theoretically be crosslinked the vinyl groups of PDMS and cholesteric LC. The structures of pure PDMS, cholesteric LC, and the crosslinked membrane were characterized with the FTIR analysis. The results were shown in Figure 1(a–c). The characteristic peaks of vinyl groups ($-CH=CH_2$) at 1603 cm^{-1} and 2980 cm^{-1} for PDMS completely disappeared in the FTIR spectra of the crosslinked membrane, suggesting that the vinyl groups of PDMS reacted with the silicon-hydrogen groups of polymethylhydrosiloxane. Compared with that of the crosslinked membrane, the intensities of the characteristic peak for the cholesteric LC at 1600 cm^{-1} ($-CH=CH_2$) almost disappeared, suggesting that the vinyl groups of cholesteric LC nearly reacted to completion with the silicon-hydrogen groups of polymethylhydrosiloxane by addition reaction. In addition, Si—C—C—Si bonds (characteristic peak at 1374 cm^{-1} and 787 cm^{-1}) were formed in the crosslinked membrane. The synthesis reactions of the crosslinked membrane were shown in Scheme 1.

Mechanical performance of the membranes

We have also examined the mechanical performance of the crosslinked membrane with various LC contents to gain further insight into the structure-property relationships. The results were given in Table I. The strain and stress values of the crosslinked membranes containing 11-alkenoic acid LC group increased significantly with increasing LC content up to 0.43% and 34.65 MPa at 5.0 wt % (mass percentage), respectively. Above this content, the



Scheme 1 Preparation of the LC/PDMS crosslinked membrane material.

TABLE I
Mechanical Performances of the Crosslinked Membrane with Different 11-Alkenoic Acid LC Contents

LC content wt %	Strain at break %	Stress at break MPa	Elastic MPa
0	0.4019 ± 0.0002	7.7060 ± 0.0003	5.8069 ± 0.0002
2.5	0.4216 ± 0.0003	12.2064 ± 0.0001	4.9848 ± 0.0003
5.0	0.4311 ± 0.0001	34.6457 ± 0.0002	4.7345 ± 0.0002
7.5	0.3978 ± 0.0002	27.2484 ± 0.0003	2.1457 ± 0.0004
10.0	0.3213 ± 0.0004	21.5623 ± 0.0002	1.8143 ± 0.0002
12.5	0.2421 ± 0.0005	15.2451 ± 0.0004	1.1746 ± 0.0003

mechanical performance decreased sharply, reaching 0.24% and 15.25 MPa at 12.5 wt %, respectively. It was clear that elongation of the crosslinked membrane decreased markedly by increasing the LC content. The crosslinked membranes with a LC content greater than 15 wt % were very brittle, and free-standing films could not be obtained. The significant dependence of elongation on the LC content of the crosslinked membrane was consistent with the structural features that the crosslinked PDMS chains were covalently bonded with increasing LC content. In addition, the strain and stress values of the LC/PDMS crosslinked membrane were higher than those of the nonmodified PDMS membrane (LC content was 0%).

The mechanical performances of the crosslinked membrane with different LCs (listed in Table II) were also discussed. It could be seen from the table that the strain and stress values of the crosslinked membranes increased with increasing the length of substitution-group in LC molecule, whereas the elongation of the crosslinked membranes decreased gradually. Therefore, we can speculate that the length of substitution-group in the LC/PDMS crosslinked membranes has influence on permeation property of the membranes.

Liquid crystal behavior

The LC behaviors of the cholesterol ester were characterized by using DSC and polarized light microscopy with a hot stage. The results indicated that the cholesterol esters had cholesteric LC behavior. For example, the LC behavior of 11-alkenoic acid cholesterol ester in polarized microscopy was as follows (showed in Fig. 2). At room temperature, the sample showed feeblish crystalline double refraction. When the sample was heated to 78.6°C, it began to flow and present chain texture, which was the typical texture of cholesteric LC. When the sample was heated to 84.9°C, the viewing field of the sample, which transitioned into an isotropy liquid state, became dark. When the sample was gradually cooled to 81°C, it came into liquid crystalline state [showed in Fig. 2(a)]. As the temperature of the sample decreased gradually, the liquid crystalline flow appeared to have a helix texture, and the sample displayed obvious helix texture with rose shapes at 72°C [showed in Fig. 2(b)]; the texture was also typical texture of cholesteric LC. When the sample was cooled further to 68°C, it displayed a fan-shaped texture with smectic LC, and crystallized slowly between 55°C and 30°C.

DSC curves of the 11-alkenoic acid cholesterol ester were showed in Figure 3, and the thermal transition of the cholesterol ester was tested and listed in Table III. As shown in Figure 3(b) (cooling curve), the exotherm peak at 64.9°C was a transition peak from the cholesteric phase to the smectic phase, resulting in a lower enthalpy value. Because the cholesterol ester crystallized slowly between 55°C and 30°C, the crystalline peak did not appear in the cooling curve. In addition, the enthalpy value of melting point peak in the second heating [Fig. 3(c)] was smaller than that of the first heating [Fig. 3(a)]. And the enthalpy value of the clean and bright point peak changed some, affirming that the sample did not completely crystallize when cooling to 50°C. Compared with the heating curve of the sample, the cooling curve had a transition peak related to the changes from the cholesteric phase to the smectic phase. The other cholesterol esters had cholesteric LC behavior similar to 11-alkenoic acid cholesterol ester.

TABLE II
Mechanical Performances of the Crosslinked Membrane Containing Different LC Groups

LC/PDMS crosslinked membrane	Strain at break %	Stress at break MPa	Elastic MPa
Non-modified PDMS membrane	0.4019 ± 0.0002	7.7060 ± 0.0003	5.8069 ± 0.0002
vinylacetic acid cholesterolic LC/ PDMS membrane	0.4108 ± 0.0004	28.4579 ± 0.0002	5.6756 ± 0.0004
4-pentenoic acid cholesterolic LC/ PDMS membrane	0.4217 ± 0.0001	30.2458 ± 0.0005	5.4289 ± 0.0002
3-hexenoic acid cholesterolic LC/ PDMS membrane	0.4235 ± 0.0003	32.2873 ± 0.0007	5.1410 ± 0.0004
11-alkenoic acid cholesterolic LC/ PDMS membrane	0.4311 ± 0.0005	34.6457 ± 0.0006	4.7345 ± 0.0003

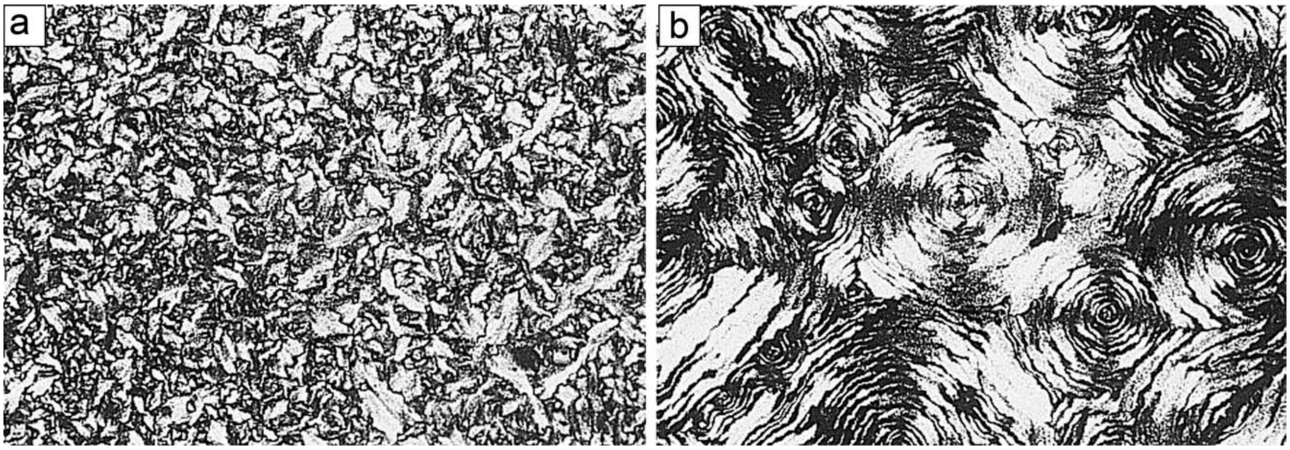


Figure 2 Liquid crystal figures of 11-alkenoic acid cholesterol ester (a, heating to 81°C; b, cooling to 72°C).

Effect of substitution group on permeation property

By introducing different cholesteric LCs (such as vinylacetic acid cholesterol ester, 4-pentenoic acid cholesterol ester, 3-hexenoic acid cholesterol ester and 11-alkenoic acid cholesterol ester) into PDMS containing vinyl groups, the LC/PDMS crosslinked membranes with different substitution groups were prepared. It was reported that the effect of the structure and the steric hindrance of the spacer in polymeric membrane on the permeability and selectivity for gas was obvious.[26] Therefore, the CO_2 and N_2 permselectivity properties of the LC/PDMS crosslinked membranes with different substitution chains length were examined in the article. At different testing temperatures and pressure differences, the permeability coefficients and separation factors of the crosslinked membrane were shown in Table IV. Compared with normal PDMS, the introduction of the cholesteric LCs contributed to increased permeability coefficients and separation factors of the crosslinked membrane. As shown in Table IV, the CO_2 permeability coefficient (P_{CO_2}) and separation factor for CO_2 and N_2 (α_{CO_2/N_2}) increased with increasing the length of substitution chains in cholesteric LC. For example, at pressure difference of 0.1 MPa and testing temperature of 40°C, P_{CO_2} and α_{CO_2/N_2} of the crosslinked membrane prepared with vinylacetic acid cholesteric LC were 4463 Barrer and 14.3, respectively. P_{CO_2} and α_{CO_2/N_2} of the crosslinked membrane prepared with 11-alkenoic acid cholesteric LC increased to 4667 Barrer and 20.1, respectively. The structure of 11-alkenoic acid cholesteric LC has seven more methylenes than that of vinylacetic acid cholesteric LC. However, the P_{CO_2} and α_{CO_2/N_2} of the crosslinked membrane prepared by 11-alkenoic acid cholesteric LC increased to 204 Barrer and 5.8, respectively. It is interesting to note that the presence of methylene units in the cholesteric LC can enhance chain flexibility. In general, when cholesterol ester is the LC phase, the chain flexibility of the LC molecular is increased with an increasing of the methylenes in cholesterol ester. Hence, cholesteric LC with more methylenes in the crosslinked membrane leads to softer molecular chains and higher permselectivity in the membrane.[20]

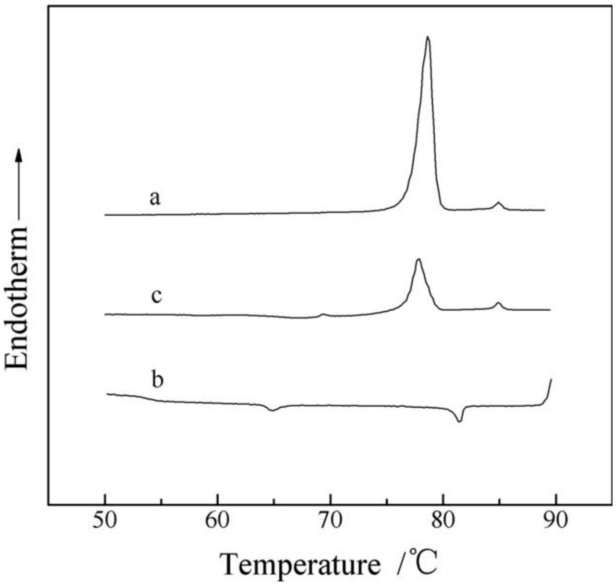


Figure 3 DSC curves of 11-alkenoic acid cholesterol ester (a) the first heating; (b) the first cooling; (c) the second heating.

Effect of pressure difference on permeation property

The influences of pressure differences on the permeation coefficients and separation factors of the crosslinked membrane containing vinylacetic acid cholesteric LC were shown in Figure 4. As observed from the figure, the P_{CO_2}-Δp, P_{N_2}-Δp, and $\alpha CO_2/N_2$-Δp curves exhibited horizontal lines, to some extent, indicating that the permeability coefficients and separation factors of the crosslinked membranes were independent

TABLE III
Phase Transition Temperatures and Enthalpy Values of the LC Samples (K, crystalline; S, smectic; Ch, cholesteric; I, isotropic)

	Phase transition temperature (°C)					
Heating and cooling process	K − S	S − Ch	Ch − I	ΔH_m (J g^{-1})	ΔH_s (J g^{-1})	ΔH_i (J g^{-1})
The first heating	65.7		73.1	42.46		1.02
The first cooling		56.4	68.2		−0.35	−1.40
The second heating	64.5		69.5	11.30		1.01

of the pressure differences or decreased slightly with increasing the pressure differences. The results also reveal that their gas permeation behavior is in accord with the general solution-diffusion mechanism of Henry's type sorption. Traditionally, the behavior of gas transport through a gas separation membrane was presumably dominated by the diffusion of absorbed molecules. Stern studied gas permselectivity of silicone rubber and side group modified silicone rubber.[27] His results showed that carbon dioxide and nitrogen permeability coefficients were independent of the pressure differences, and that higher gas permeability of the membrane had been mainly affected by greater gas solubility in the membrane. If gas permeation through polymeric membrane is in accord with the general solution-diffusion mechanism of Henry's type sorption, gas permeability coefficient is related to solubility coefficient and diffusion coefficient and unrelated to the upstream pressure difference.

Effect of testing temperature on permeation property

Table IV examined the effect of the testing temperature on P_{CO_2} and $\alpha CO_2/N_2$ of the crosslinked membranes containing 4-pentenoic acid cholesteric LC. Referring to Table IV, it could be seen that P_{CO_2} increased with an increase of testing temperature under the same pressure difference. For example, under the same pressure difference of 0.05 MPa, P_{CO_2} was increased from 3419 Barrer at 20°C to 3854 Barrer at 50°C. The effect of temperature on permeability properties of the membranes was in accord with the general role of gas separation membrane. In contrast, $\alpha CO_2/N_2$ decreased with an increase of the testing temperature. Under the above conditions, $\alpha CO_2/N_2$ of the crosslinked membrane was decreased from 19.4 at 20°C to 14.0 at 50°C, which were greater than those of general modified PDMS membrane ($\alpha CO_2/N_2$ was approximately 10.0). Stern demonstrated that the effects of temperature on the permeability coefficients depended on changes in the diffusion coefficient and the solubility coefficient when they investigated structure-permeability relationships for different silicone polymers.[27] The diffusion coefficient always increased with increasing temperature, whereas the opposite trend was generally observed in the solubility coefficient.

It was interesting to examine the effects of the testing temperature on P_{CO_2} and $\alpha CO_2/N_2$ of the

TABLE IV
Effect of Some Factors on CO_2 Permeability Coefficient and CO_2/N_2 Separation Factor for the Crosslinked Membrane Containing Different LC Groups

The crosslinked membrane containing different LC	Pressure difference (MPa)	P_{CO_2} (Barrer)				α_{CO_2}/N_2			
		20°C	30°C	40°C	50°C	20°C	30°C	40°C	50°C
vinylacetic acid cholesteric LC	0.05	4011	4125	4426	5020	18.2	16.3	14.6	13.1
	0.1	3859	4262	4463	5013	18.0	16.4	14.3	13.0
	0.2	3792	4211	4427	4975	18.1	16.1	14.4	13.3
	0.3	3853	4219	4420	4968	17.9	16.0	14.7	12.9
4-pentenoic acid cholesteric LC	0.05	3419	3511	3528	3854	19.4	17.9	15.9	14.0
	0.1	3422	3480	3578	3859	19.6	17.7	16.0	13.9
	0.2	3426	3487	3535	3884	19.7	17.5	15.7	14.1
	0.3	3344	3443	3528	3811	19.0	17.4	15.8	13.6
3-hexenoic acid cholesteric LC	0.05	3475	3610	3751	4145	21.8	19.6	17.8	16.2
	0.1	3487	3604	3693	4109	20.7	19.7	17.9	15.9
	0.2	3497	3599	3757	4157	21.1	20.2	17.4	16.2
	0.3	3502	3606	3778	4105	22.0	19.2	18.0	16.2
11-alkenoic acid cholesteric LC	0.05	4235	4306	4537	5078	23.5	21.4	19.4	18.5
	0.1	4282	4356	4667	5115	24.0	22.0	20.1	18.7
	0.2	4220	4322	4578	5113	23.1	21.6	19.3	18.6
	0.3	4203	4338	4670	4998	23.6	21.9	20.4	18.9

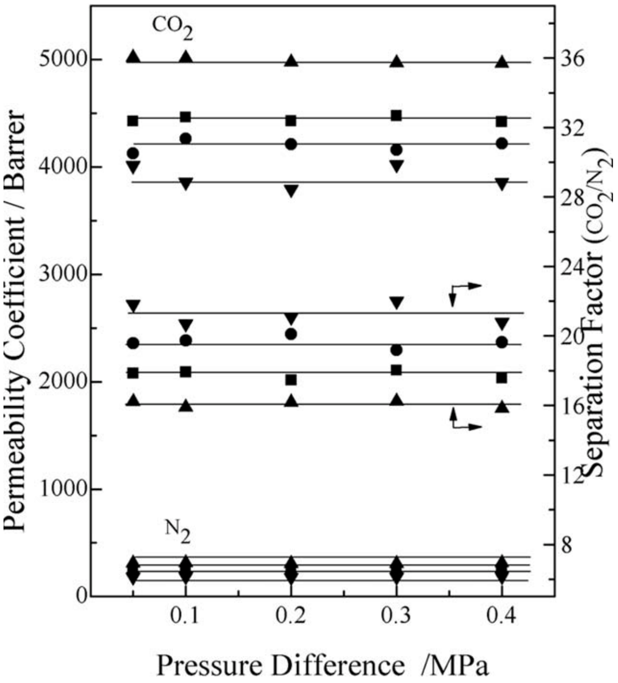


Figure 4 Effect of pressure difference on permeability coefficient for CO_2 and separation factor for CO_2 and N_2 of the LC/PDMS crosslinked membrane containing vinylacetic acid cholesteric LC (▼: 20°C; ●: 30°C; ■: 40°C; ▲: 50°C).

crosslinked membrane containing different cholesteric LCs (such as vinylacetic acid cholesterol ester, 4-pentenoic acid cholesterol ester, 3-hexenoic acid cholesterol ester and 11-alkenoic acid cholesterol ester) (shown in Table IV). As shown in the table, CO_2 permeation coefficients through different LC/PDMS crosslinked membranes were increased with an increase of the testing temperature under the same pressure difference. It should be noted that $\alpha CO_2/N_2$ was kept a line with an increase of the testing temperature.

Arrhenius curves for the different crosslinked membranes were obtained from a plot of ln P_{CO_2} as a function of 1/T (as shown in Fig. 5). At pressure difference of 0.01 MPa, the permeation activation energies for CO_2 calculated by Arrhenius curves were 7.2 kJ/mol, 6.4 kJ/mol, 5.0 kJ/mol, and 4.4 kJ/mol, respectively. Compared to the nonmodified PDMS crosslinked membrane, the permeation activation energies of the crosslinked membranes were obviously lower. The results suggested further that the crosslinked membranes for CO_2 were more permeable than normal PDMS membrane. And the permeation activation energy values of the crosslinked membranes decreased as the length of the substitution group in the membranes increased, suggesting that CO_2 could permeate easily through the crosslinked membranes with longer substitution groups.

Effect of cross-linked time on permeation property

The crosslinking reaction can shorten the space between macromolecule chains of PDMS and cholesteric LC, contributing to an increase in the fractional free volume and an increasing selectivity of the crosslinked membrane. By using covalently crosslinked method to improve permselectivity property for CO_2, the transparent and flexible LC/PDMS crosslinked membrane was prepared by using polymethylhydrosiloxane as a crosslinked agent. Clearly, chloroplatinic acid solution as the catalyst could contribute to silicone-hydrogen addition reaction and crosslinking reaction. The crosslinked membrane prepared by the method had more flexible and better mechanical strength for measuring permeation properties; the improvement in the mechanical properties was attributed to the oligomeric structure of the crosslinked agent. In addition, the vinyl chain content of PDMS was very high, but the vinyl was distributed homogeneously and nonregularly on the side groups of PDMS main chains. Compared with general crosslinked structure with C-C bonds prepared by an addition reaction, the addition reaction which was generated between the vinyl and silicone-hydrogen atom, resulted in more flexible crosslinked structure containing Si-C bonds. Therefore, the degree of crosslinked had an effect on permeation property of the crosslinked membrane. In addition, crosslinked usually leads to higher stability, however, a higher degree of crosslinked can reduce the chain mobility of the otherwise flexible siloxane linkages, which may lead to decrease in the permeance.[25,28]

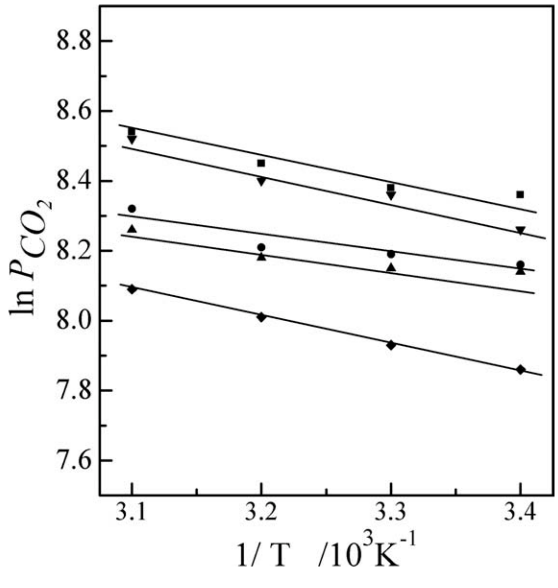


Figure 5 Arrhenius curves of different LC/PDMS membranes for CO_2 at pressure difference of 0.1 MPa (◆: nonmodified; ▲: vinylacetic acid; ▼: 4-pentenoic acid; ●: 3-hexenoic acid; ■: 11-alkenoic acid).

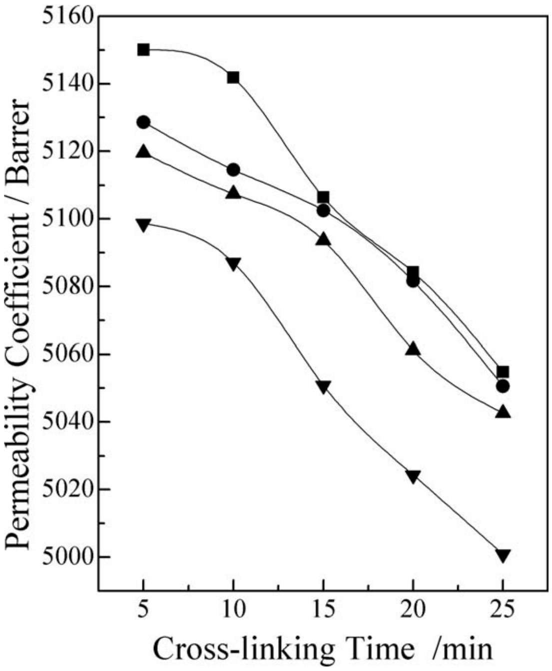


Figure 6 Effect of crosslinking time and temperature on CO_2 permeability coefficient of the membrane at pressure difference of 0.1 MPa (■: 20°C; ●: 30°C; ▲: 40°C; ▼: 50°C).

To obtain proper membrane-forming condition and higher possible permselectivity, the optimization of crosslinked time and crosslinked temperature was discussed. Figure 6 presented the effect of crosslinked time and crosslinked temperature on CO_2 permeation properties of the LC/PDMS crosslinked membrane containing 11-alkenoic acid LC at pressure difference of 0.1 MPa and testing temperature of 40°C. On the one hand, it could be seen from the figure that P_{CO_2} decreased with increasing of crosslinked times, and the value decreased sharply when the crosslinked time exceeded 20 min, especially decreased dramatically at crosslinked temperatures of 20°C and 50°C. The experimental result indicated the diffuse permeation of carbon dioxide in the membrane was more difficult with an increase of crosslinked time. On the other hand, at the same crosslinked time, P_{CO_2} decreased as crosslinked temperature increased. However, P_{CO_2} changed slightly for the crosslinked membrane prepared at the crosslinked temperature of 30°C and 40°C, as well as those with crosslinked times of 10–15 min. The findings could be explained well by the soft chain-*cross*-linked caused free-volume increase mechanism, suggesting that at shorter crosslinked times, segmental motion of PDMS macromolecule in the crosslinked membrane was not restricted because the length between adjacent crosslinked points was longer than that between segments. In addition, the reason for permeation properties can be explained by the fact that the terminal group (double bond) of LC molecule disappeared in the LC/PDMS crosslinked membrane had made PDMS molecule more flexible. However, at 20°C or 50°C, the crosslinked degree had obvious effect on the CO_2 permeability coefficient and resulted in a sharp decrease in the free volume of the membrane. It was pointed out that the introduction of siloxane linkage for polymethylhydrosiloxane as the crosslinked agent into the structure of PDMS could also enhance chain flexibility, resulting in improving permselectivity for CO_2.

Effect of LC content on permeation property

In general, permeation properties of polymeric membranes for CO_2 are more sensitive to polymeric structure than those for O_2 or N_2 gas with a low polarity. Hence, it is expected that the gas separation performance of the crosslinked membrane would be further enhanced by introducing cholesteric LC group into side-chains of PDMS, resulting in the increased rigidity of the PDMS backbone and the increased free volume available for gas molecules. In addition, the PDMS segments modified by LC groups with flexible chains could provide large free volume. And the nature of the crosslinked membrane with the flexible chain structure was in favor of the transportation of each gas. Therefore, for the LC/PDMS crosslinked membrane, it could be affirmed that the LC content appeared to have a great influence on the permeability. In particular, the LC with reactive end groups had effect on both the membrane ingredient, the structure morphology and the crosslinked degree of the crosslinked membrane.

At pressure difference of 0.1 MPa and testing temperature of 40°C, the effects of the 11-alkenoic acid LC content on CO_2 permeation properties of the LC/PDMS crosslinked membrane were showed in Figure 7. With increasing LC content in the membrane, the P_{CO_2} displayed an increase, which was followed by a decrease. And P_{CO_2} had a maximum value when the LC content in the membrane reached approximately 5.0 wt.% (mass percentage). For example, the P_{CO_2} of the crosslinked membrane increased significantly, from 4632 Barrer to 5114 Barrer, when the LC content increased from 2.5 wt.% LC to 5.0 wt.% LC, this value decreased to 3400 Barrer at a LC content of 12.5 wt.%. In addition, the rigid LC framework in the membrane hindered the movements of the PDMS chains. Hence, a higher LC content leads to greater restriction of these movements and lower P_{CO_2} of the membrane. When the LC content was up to 20 wt.%, the crosslinked membrane was not be obtained, which was consistent with the mechanical properties discussed above. These results indicated that the crosslinked method and the introduction of the LC group could be beneficial factors for the gas permselectivity.

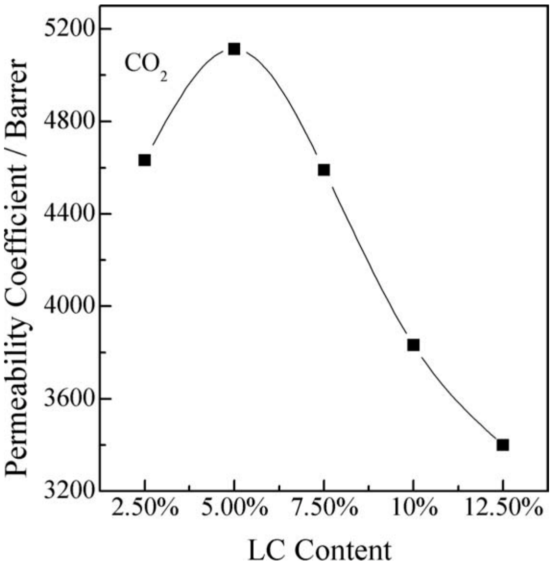


Figure 7 Effect of content of LC on CO_2 permeability coefficient of the membrane at pressure difference of 0.1 MPa and testing temperature of 40°C.

The experimental results could also be explained well as follows. On the one hand, the rigidity of PDMS chain had effect on permeation property of crosslinked membrane. It is generally agreed that gas permeability through compact polymer membranes is related to chemical structure and aggregated structure of membrane material. An increasing of LC content in the crosslinked membrane could reduce the number of —Si—O— constitutional unit in PDMS chains, resulting in increasing space interaction between LC group and PDMS group, increasing rigidity of PDMS chains and CO_2 permeability coefficient of the crosslinked membrane. On the other hand, when LC content exceeded 5.0 wt %, the structural configuration and the crosslinked degree of the membrane changed as LC content increased. In particular, when the content of LC exceeded 10.0 wt %, the brittleness of the membrane obviously increased and the crosslinked degree decreased obviously. These factors would result in a decrease in CO_2 permeability coefficient of the crosslinked membrane.

CONCLUSIONS

In summary, we have developed a novel LC/PDMS crosslinked membrane material prepared by silicone-hydrogen addition reaction. The permeation properties and gas separation of the membrane were enhanced owing to the introduction of LC with soft structure into the PDMS membrane. For example, at pressure difference of 0.1 MPa and testing temperature of 40°C, P_{CO_2} and $\alpha CO_2/N_2$ of the crosslinked membrane reached 4667 Barrer and 20.1, respectively. The introduction LC groups into PDMS played a more important role in the improvement of permselectivity properties. The experimental results showed that permselectivity of the crosslinked membranes varied with the content of incorporated LC and the length of substitution-group in the membrane. CO_2 permeability coefficients were increased with LC content, then decreased with LC content up to 5.0 wt %. When LC content in the membrane was 5.0 wt %, the crosslinked membrane had better membrane-forming property, higher CO_2 permeability coefficient and comparatively higher CO_2/N_2 selectivity. Of course, P_{CO_2}, P_{N_2} and $\alpha CO_2/N_2$ of the membrane were independent of the pressure differences, revealing that gas permeation behavior of the membrane was in accord with the general solution-diffusion mechanism of Henry's type solution. In addition, CO_2 permeability coefficient decreased with increasing of crosslinked time and decreased sharply when the crosslinked time exceeded 20 min. Therefore, we believe that the introduction of LC into PDMS membrane and a proper crosslinked method can enhance obviously permeation properties of the modified membranes.

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