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Facile Synthesis of an Amphiphilic 1,3,5-Trisubstituted Benzene as a Novel Surface Modifier by Selective Photocyclic Aromatization and Efficient Improvement of Oxygen Permselectivity by the Addition of the Surface Modifier

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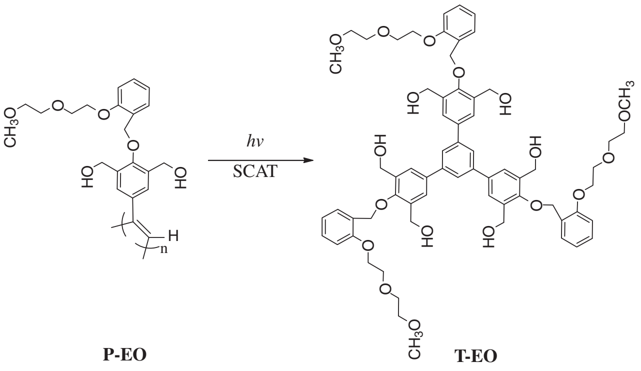
An amphiphilic 1,3,5-trisubstituted benzene as a new 2D surface modifier (T-EO) which has six hydroxy groups and three oligoethylene groups was successfully and easily synthesized by selective photocyclic aromatization in high conversion and selectivity for the first time. We prepared four kinds of blend membranes based on PVA or poly(trimethylsilylphenylacetylene) (poly(SPA)) containing the new amphiphilic cyclic trimer (T-EO) or the corresponding polymer (P-EO), that is, T-EO/PVA, P-EO/PVA, and T-EO/poly(SPA) membranes prepared by conventional solvent casting method (Method I) and T-EO/poly(SPA) membranes prepared by a new solvent casting method (Method II). T-EO/PVA membranes by Method I and T-EO/poly(SPA) membranes by Method II showed better performance in oxygen permeation than P-EO/PVA membranes by Method I and T-EO/poly(SPA) membranes by Method I, respectively. A PVA-based membrane containing 1.0 wt % T-EO showed the best performance, that is, the α became twice that of the original PVA membrane without any decrease in P_{O_2}. The ideal improvement may be caused by effective surface modification by T-EO.

Permselective membranes separating gases such as oxygen and nitrogen are very useful for many practical solutions to environmental and energy problems. Hence, many studies have been reported on such membranes from not only organic polymers but also inorganic compounds.[1] The requirements for oxygen permselective membranes are (1) high permeability coefficient (P_{O_2}: $cm^3(STP)\,cm\,cm^{-2}\,s^{-1}\,cmHg^{-1}$), (2) high separation factor ($\alpha = P_{O_2}/P_{N_2}$), and (3) good membrane forming ability (high mechanical strength). However, these three characteristics have been unobtainable at the same time in almost all membrane materials reported. For example, membranes having higher P_{O_2} had lower α and membranes having higher α had lower P_{O_2}, that is, P_{O_2} and α showed a tradeoff relationship.[1a] Also membranes having higher P_{O_2} tended to be too flexible and membranes with higher α tended to be too brittle.

To overcome the above problems, that is, to obtain materials satisfying the three requirements simultaneously, we reported surface modifications of conventional polymer membranes with sufficient mechanical strength by solvent casting a mixture of small amounts of surface active polymers and conventional base polymers.[2] It was an effective method to enhance α with a small decrease in P_{O_2} without change to the good membrane forming abilities of the base polymers. The enhancement of α, however, was not sufficient.



Scheme 1. Selective photocyclic aromatization (SCAT) of P-EO.

In this study, to improve effectiveness of the surface modifiers, a new surface active compound, T-EO (Scheme 1) was designed. T-EO is a 1,3,5-trisubstituted benzene derivative which has triphenylbenzene as a hydrophobic planer (2D) core and three *ortho*-substituted oligo(ethylene oxide) groups as hydrophilic regions and in addition it has six hydroxy groups which can form hydrogen bonds. If T-EO was used as a surface modifier of hydrophilic polymer membranes, the hydrophilic surface exposed by hydrophobic air can be covered by the hydrophobic 2D part of T-EO, because the triphenylbenzene portion tends to accumulate on the surface and the oligo(ethylene oxide) groups can work as an anchor segment. In addition, if the six hydroxy groups form hydrogen bonds between the molecules, a planar i.e., 2D supramolecular surface can be formed. However, since the molecular structure of T-EO is complicated and has three kinds of functional groups, it is difficult to obtain it in a high yield by a simple synthetic route. For example, the direct cyclization from EO (Scheme S1)[3] to T-EO is difficult because the catalyst for the direct cyclization reaction has low functional group tolerance.

We found and reported recently a novel polymer reaction called SCAT (highly selective photocyclic aromatization) reaction.[4] The SCAT reaction has many advantages.[4a] Among the advantages, high conversion, high selectivity, and simple procedure (only light irradiation) are very useful for synthesis of T-EO and therefore we selected SCAT as the synthetic route. In this communication, a facile synthesis of T-EO by the SCAT reaction and enhancement of α by surface modification by using T-EO are reported.

T-EO was obtained quantitatively and easily by light irradiation (SCAT) on P-EO without any purification. For the

Table 1. Oxygen permeation and contact angles of four kinds of blend membranes

No.	T-EO[a] Or P-EO	T-EO/PVA (Method I)			P-EO/PVA (Method I)		
		P_{O_2}[b]	α[c]	θ[d]	P_{O_2}[b]	α[c]	θ[d]
1	0	13.7	1.71	39.1	13.7	1.71	39.1
2	0.060	13.5	1.80	40.4	—	—	—
3	0.50	13.7	2.68	40.1	—	—	—
4	1.0	12.7	3.88	40.4	12.9	2.15	42.2
5	5.0	8.8	3.73	51.5	8.8	2.25	30.2
6	10	5.1	4.11	53.1	4.9	3.82	34.2

No.	T-EO[a]	T-EO/poly(SPA) (Method I)			T-EO/poly(SPA) (Method II)		
		P_{O_2}[e]	α[c]	θ[d]	P_{O_2}[e]	α[c]	θ[d]
7	0	171	2.36	106	171	2.36	106
8	0.50	150	2.45	105	142	2.58	100
9	1.0	136	2.55	107	128	2.88	95
10	5.0	120	2.63	104	111	3.22	87

[a]In wt %. [b]In 10^{-13} cm^3(STP) cm cm^{-2} s^{-1} cmHg^{-1}. [c]$\alpha = P_{O_2}/P_{N_2}$. [d]Contact angles of water droplets on the air surface of the blend membranes (°). [e]In 10^{-10} cm^3(STP) cm cm^{-2} s^{-1} cmHg^{-1}.

experimental details, procedures, and results of synthesis of the monomer (EO), the polymer (PO), and the cyclic trimer (T-EO), see the Supporting Information.[3] T-EO was used as a 2D surface modifier and three kinds of blend membranes containing T-EO were prepared. The blend membranes were prepared by the following two methods: Method I (conventional method): A toluene solution of the polymer and 0.060–5.0 wt % of the additives was cast on a poly(tetrafluoroethylene) sheet. Method II (new method): A toluene solution of poly(trimethylsilylphenylacetylene) (poly(SPA)) and a methanol solution of T-EO was first blended together, and then the solution was cast on a poly(tetrafluoroethylene) sheet. Oxygen and nitrogen permeability coefficients (P_{O_2}, and P_{N_2}: cm^3(STP) cm cm^{-2} s^{-1} cmHg^{-1}) were measured by gas chromatography at 25 °C using YANACO GTR-10.

A 1,3,5-trisubstituted benzene (T-EO: Scheme 1) which has six hydroxy groups and three oligoethylene groups was synthesized successfully for the first time by a selective photocyclic aromatization (SCAT) method we developed and reported recently.[4a] In addition, the conversion and selectivity were very high, and the procedure was pretty simple, that is, only light irradiation to the corresponding polymer membrane. Four kinds of blend membranes containing T-EO were prepared by using the two methods. One was conventional method (Method I) using one solvent which can solve the base polymer and the additives, and the other was newly developed method (Method II) using two solvents which were miscible but have different solubilities for the base polymer and the additive (T-EO) and different boiling points. Oxygen permeation behavior (P_{O_2} and $\alpha = P_{O_2}/P_{N_2}$) through the resulting four kinds of blend membranes were measured. The results were shown in Table 1 and Figure 1.

As shown in Table 1, Nos. 1 and 4 and Figure 1A, the α values of T-EO/PVA blend membranes (●) increased steeply from 1.71 to 3.88 without any drop in P_{O_2} when only 1.0 wt % of the cyclic trimer (T-EO) was added. On the other hand, by adding the same amount (1.0 wt %) of the corresponding polymer (P-EO) into the PVA membrane (■), the permselectivity showed almost no change. By increasing the content of T-EO from 1.0 to 10 wt % in T-EO/PVA blend membranes, the permselectivity had almost no change but the permeability decreased markedly (Figure 1A and Table 1). In summary, the PVA-based blend membrane containing 1.0 wt % of T-EO had the best performance and the small addition of T-EO to PVA was effective for enhancing the permselectivity of the PVA membranes without any drop in P_{O_2}.

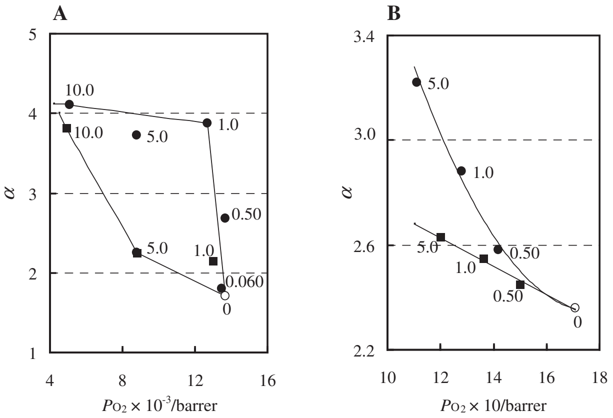


Figure 1. Relationship between the P_{O_2} and α of the blend membranes (the numbers in the figure are the content of additives (wt %)). A: ●: T-EO/PVA blend membranes; ■: P-EO/PVA blend membranes. B: ■: T-EO/poly(SPA) blend membranes prepared by Method I; ●: T-EO/poly(SPA) blend membranes prepared by Method II (1 barrer = 10^{-10} cm^3(STP) cm cm^{-2} s^{-1} cmHg^{-1}).

The T-EO (5.0 wt %)/poly(SPA) membranes (●) prepared by Method II we developed showed a higher permselectivity compared with the ones (■) having the same content of T-EO by Method I (Figure 1B and Table 1). The permselectivities of the membranes prepared by Method II increased more than those by Method I although the decreases in permeability were almost the same (Figure 1B and the lower lines of Table 1). In summary, we measured oxygen permeation through the two kinds of T-EO/poly(SPA) blend membranes prepared by the two methods I and II. As a result, the membranes prepared by Method II showed a better performance on enhancing the permselectivity compared with the ones prepared by Method I.

In conclusion, by comparing these four kinds of membranes above-mentioned, we conclude that the PVA-based membrane containing 1.0 wt % T-EO on the surface was the best judging from the performance and the degree of improvement.

To determine the reason for the effective improvement of the α values without large drops in P_{O_2} described above, we investigated the surfaces of the blend membranes by measuring contact angles (θ) of water droplets. The results are shown in Figure 2 and Table 1.

Judging from the θ values in Figure 2A and the upper part of Table 1, Nos. 1–6, the surface of T-EO/PVA blend membranes (●) became more hydrophobic than the original pure polymer membrane (PVA) but the surface of P-EO/PVA blend

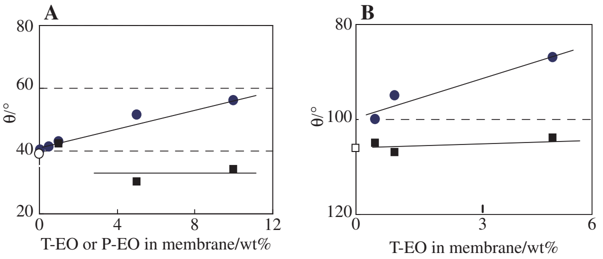


Figure 2. Plots of contact angles vs. the content of additives in the blend membranes. A: ●: T-EO/PVA blend membranes; ■: P-EO/PVA blend membranes. B: ■: T-EO/poly(SPA) blend membranes prepared by Method I; ●: T-EO/poly(SPA) blend membranes prepared by Method II.

membranes (■) did not become more hydrophobic. Therefore the surface of T-EO/PVA blend membranes were more effectively modified by the newly synthesized additives (T-EO) than those of P-EO/PVA blend membranes. In addition, as described above, T-EO/PVA blend membranes showed much better oxygen permselectivity than P-EO/PVA blend membranes (Figure 1A). Therefore, the effective improvement and good performance of T-EO/PVA blend membranes are thought to be caused by the effective surface-modification by T-EO.

In the case of addition of 5.0 wt % of T-EO or P-EO to PVA, they showed almost the same P_{O_2} but the former membrane showed about twofold higher α than the latter as described above (Figure 1A) and simultaneously the θ value of the former membrane was higher than that of the latter (Table 1, No. 5, and Figure 2A). Therefore, the modified surface can be one of the reasons for the effective enhancement of α. The difference between T-EO and P-EO may be caused by the difference of their molecular assembly structures on the surface. It may mean T-EO is a good 2D surface modifier. Especially in the case of addition of 1.0 wt % of T-EO to PVA, the blend membrane showed about twice higher α than the original pure PVA membrane with almost no drop in P_{O_2} (Figure 1A). It may also be caused by effective surface modification although no clear change in θ value was observed. It is thought to be that the surface was modified very effectively and no alternation of the inside or bulk structure of the blend membrane and as a result only α was increased and no drop in P_{O_2} was observed.

Judging from the θ values in Figure 2B and the lower part of Table 1, Nos. 7–10, the surface of T-EO/poly(SPA) blend membranes prepared by Method II which was developed in this study became more hydrophilic than the original pure polymer membrane (poly(SPA)) but the surface of T-EO/poly(SPA) blend membranes prepared by Method I (conventional method) did not become more hydrophilic. Therefore, the surfaces of T-EO/poly(SPA) blend membranes prepared by Method II were more effectively modified by the newly synthesized additives (T-EO) than those by Method I. It was unusual that the surfaces were modified by more hydrophilic additives by Method II. We have achieved such unusual modification by Method II. The reason for the success is not clear at present but we speculate the reason as follows: The point is the difference of the boiling points (bp's) of the two solvents used. Since the more hydrophilic solvent (methanol) having a lower bp, which is evaporating first, has higher solubility for T-EO, which is more hydrophilic than poly(SPA), T-EO could be accumulated at the surface. As we described above, T-EO/poly(SPA) blend membranes prepared by Method II showed better performances of oxygen permselectivity than those by Method I (Figure 1B). Therefore, the effective improvement and good performance in oxygen permeation of T-EO/poly(SPA) blend membranes prepared by Method II are thought to be caused by the effective surface-modification.

In conclusion, we reported the four kinds of blend membranes based on PVA or poly(SPA) containing the new amphiphilic cyclic trimer (T-EO), which was simply prepared in a high yield by SCAT reaction, developed previously by us, of the corresponding polymer (P-EO), that is, T-EO/PVA, P-EO/PVA, and T-EO/poly(SPA) membranes prepared by conventional solvent casting (Method I) and T-EO/poly(SPA) membranes prepared by a new solvent casting method we developed (Method II). T-EO/PVA membranes prepared by Method I and T-EO/poly(SPA) membranes prepared by Method II showed better performance in oxygen permeation than P-EO/PVA membranes prepared by Method I and T-EO/poly(SPA) membranes prepared by Method I, respectively. Especially the 1.0 wt % of T-EO containing PVA-based membranes showed the best result, because the α became twice that of the original PVA membrane without any decrease in P_{O_2}. The ideal improvement may be caused by effective surface modification by T-EO. Since T-EO has a planer region in its molecule, it can arrange in 2D manner on the surface. The 2D supramolecular surface may improve the performance. Further investigation about surface structures are now in progress.

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