Optical Resolution through Cellulose Acetate Membranes

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Developing novel membrane materials for optical resolution is an important objective with applications in the pharmaceutical industry, food preparation, agricultural chemicals, and so forth. Optical resolution with a permselective membranes is an attractive technique for separating optically active compounds since it offers continuous operation, as well as simplicity and energy efficiency compared with the conventional optical resolution methods. From the reported results for optical resolution with polymeric membranes, it can be deduced that the introduction of a chiral microenvironment at the molecular recognition site in the synthetic membrane is indispensable for the membranes to show optical resolution. However the preparation of suitable molecular recognition compounds for incorporation into synthetic membranes may be

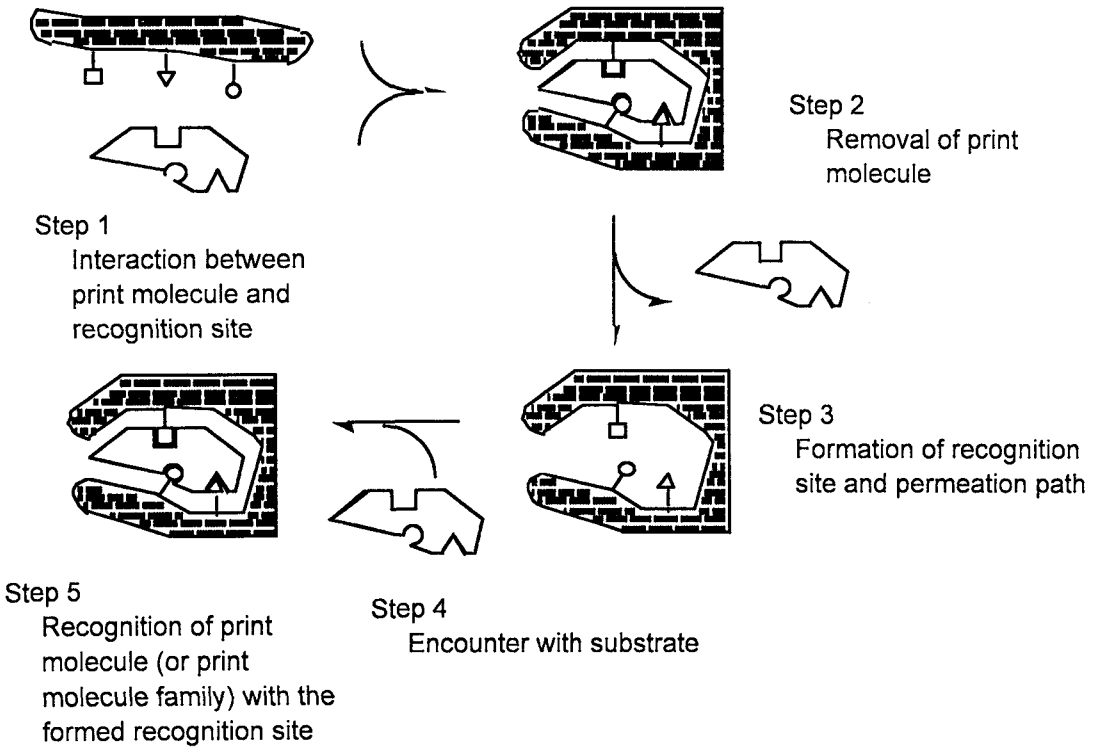

Fig. 1 Concept of alternative molecular imprinting.

synthetically challenging.

Molecular imprinting[1] is another promising method for the introduction of chiral recognition site into synthetic membranes. This approach has been applied to the membrane separation[2-4]. In that technique, functional monomers, forming covalent or non-covalent bonds with the print molecule, are radically polymerized so that specific recognition sites toward the target molecule can be introduced into the cross-linked polymers. As mentioned above, the molecular imprinting technique is the most easiest way to generate synthetic macromolecules with molecular recognition ability. However, the molecularly imprinted polymeric materials, prepared by conventional molecular imprinting, are not reusable. In other words, once the molecularly imprinted materials, of which recognition site is prepared for the recognition of a given target molecule, falls in disuse, such a material cannot be applicable to the recognition of other molecule, and will do nothing but will be discarded. In addition to this, diversity of molecularly imprinted materials is not expected by applying conventional molecular imprinting technique, even though it was a pioneering methodology. Based on this, the authors' research group has proposed another method since 1994[5], which has been named an alternative molecular imprinting technique (Fig. 1). Contrary to the conventional molecular imprinting, molecular recognition sites are formed at the same time as the molecular imprinting materials are prepared from the polymer solution. This implies that molecular recognition sites can be introduced in various materials, such as oligopeptide derivatives[6], derivatives of natural polymer[7], and synthetic polymers[8]. In addition to this, as expected from the formation mechanism of imprinted materials, once the molecularly imprinted polymer, which was prepared for the recognition of a given target molecule by applying an alternative molecular imprinting technique, falls in disuse, the imprinted polymer can be dissolved and converted into another molecular recognition material by adopting a different target molecule as a print molecule. In other words, molecularly imprinted polymeric materials prepared by our method can be reusable.

Fig. 2 shows the dependence of adsorption of racemic Glu in the imprinted CA membranes. The results for Z-D-Glu imprinted CA membranes are shown in Fig. 1 (a) and those for Z-L-Glu imprinted CA membranes in Fig. 2 (c). In Fig. 2, the amounts of adsorbed Glu by the membrane are given in relative one, which were converted to those of a single repeating unit of D-glucose ring basis.

These two membranes show adsorption selectivity (i.e., give chiral recognition). The membrane imprinted by Z-D-Glu recognizes the D-isomer in preference to the corresponding L-isomer, and that imprinted by Z-L-Glu recognizes the L-isomer in preference to the D-isomer. The adsorption selectivities for both membranes ($S_{A(i/j)}$) increase from 1.2 tp 2.3 with the decrease in the molecular imprinting conditions from 3.0 to 0.5. In the Z-D-Glu imprinted membranes, the excess amount of D-Glu preferentially adsorbed by the membarne was 0.29 times that of the D-glucose ring in the membrane. In the L-isomer imprinted membrane, the excess amount was 0.31 times of the D-glucose ring in the membrane.

From the adsorption isotherms for those two kinds of imprinted membranes, it was made clear that L-Glu in the Z-D-Glu imprinted membrane and D-Glu in the L-isomer imprinted membrane were adsorbed in the membrane without any specific interaction with the imprint site. On the other hand, the adsorption isotherms of D-Glu in D-isomer imprinted membrane and that of L-Glu in the L-isomer imprinted membrane consist of non-specific adsorption combined with adsorption on specific recognition sites towad the same print

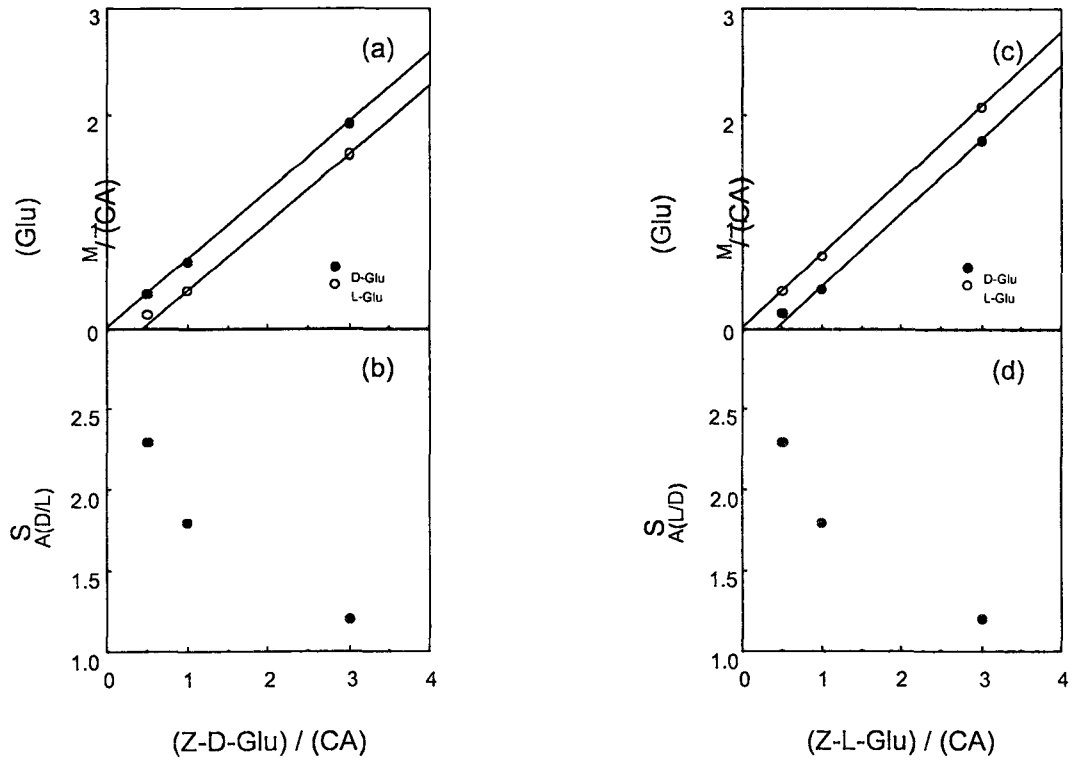

Fig. 2 Effect of the membrane preparation condition on Glu adsorption (a), and on adsorption selectivity toward D-Glu (b) of the membrane imprinted by Z-D-Glu, and that on Glu adsorption (c), and on adsorption selectivity toward L-Glu (d) of the membrane imprinted by Z-L-Glu.

molecule family, which has the same absolute configuration as the print molecule.

Electrodialysis of racemic Glu was studied as one of the application of the present molecularly imprinted CA membranes to membrane separation. It is of interest to permeate D- and L-Glu simultaneously from a racemic feed solution. That is, the feed side, middle chamber (M), of the sketch in Fig. 3, is laid out in between two permeate sides. The L-Glu selective adsorption membrane, which was imprinted by Z-L-Glu, was mounted between the L and the M sides, and the D-Glu selective adsorption membrane was mounted between the M and R sides. The time transport curves for dual direction enantioselective electrodialysis are shown in Fig. 3. As can be seen, L-Glu was transported preferentially to the L side and the D-Glu was transported simultaneously to the R side.

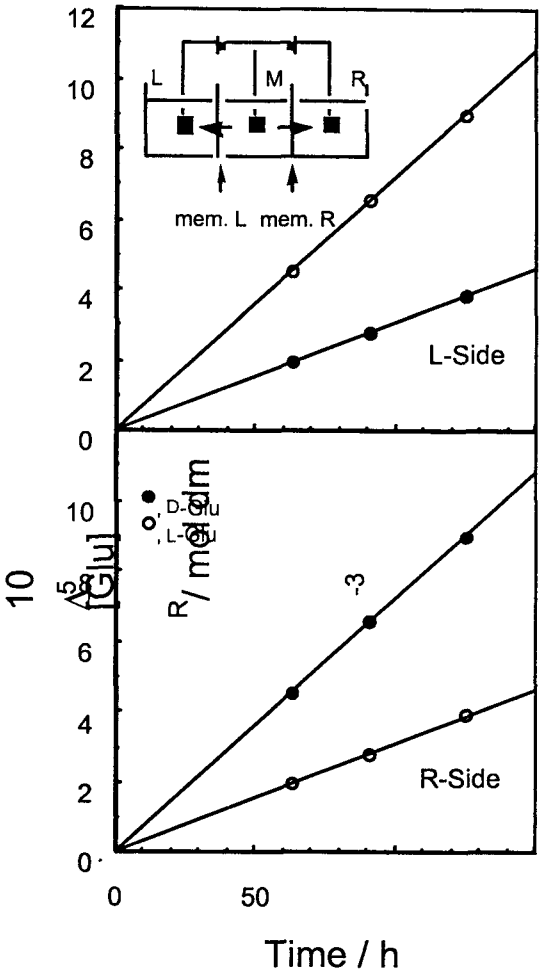

Fig. 3 Time-transport curves of D- and L-Glu by dual direction electrodialysis at ΔE = 2.5 V through molecularly imprinted CA membranes. [(Z-L-Glu) / (CA) = (Z- D-Glu) / (CA) = 0.5.]

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