

# Specialty Polymeric Membranes. XIV. Pervaporation of Benzene/Cyclohexane Mixtures through Modified Polyamide Membranes

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**ABSTRACT:** Methyl methacrylate, ethyl methacrylate, propyl methacrylate, and styrene were graft-polymerized onto the amorphous polyamide poly(hexamethylene terephthalamide/isophthalamide) (SELAR). Membranes were prepared from the modified SELAR and unmodified SELAR. The membranes were permeated benzene in preference to

cyclohexane from benzene/cyclohexane mixtures by pervaporation. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 183–188, 2003

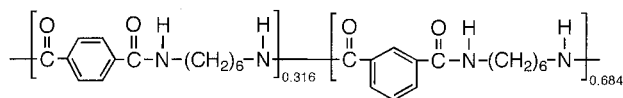
**Key words:** graft copolymers; membranes; selectivity; separation technique

## INTRODUCTION

The separation of petroleum components has been performed with energy-intensive processes, such as rectification, azeotropic distillation, extractive distillation, and solvent extraction. Membrane separation is recognized as a potentially more economical alternative for such separation techniques. Pervaporation<sup>1,2</sup> is one of the most promising membrane separation processes for petroleum refining. The separation of aromatics and aliphatics into an aromatic-rich permeate, which is employed for high-octane-number gasoline, and into an aromatic-lean retentate, which is used for diesel, is one interesting membrane separation process in petroleum refining in connection with environmental issues.<sup>3</sup> Many articles have reported on the pervaporation separation of benzene/cyclohexane mixtures, both components being top 50 chemicals,<sup>4</sup> with synthetic polymeric membranes.<sup>5–53</sup> As described previously,<sup>43</sup> membrane materials for petroleum refining should be chosen from commercially available common polymers or common polymers chemically modified without complicated modification reactions because large volumes of mixtures should be treated by the prepared membrane. To this end, nylon 6,<sup>25,27,44,48,51</sup> polyamide–polyether block copolymer,<sup>38</sup> poly(vinyl chloride),<sup>43</sup> poly(vinyl alcohol),<sup>45</sup> polysulfone,<sup>47</sup> and poly(vinylidene chloride-co-vinyl chloride)<sup>52</sup> have been adopted as membrane materials, and the pervaporation performances of membranes from

modified and unmodified polymers have been investigated.

In this study, the amorphous polyamide poly(hexamethylene terephthalamide/isophthalamide) (SELAR) was adopted as another membrane material:



## SELAR

Novel membrane materials were prepared by the radical graft polymerization of various monomers onto the parent polyamide (SELAR). The pervaporation of benzene/cyclohexane mixtures, through modified and unmodified SELAR membranes, was investigated.

## EXPERIMENTAL

### Materials

SELAR (6T/6I = 31.6/68.4 mol/mol) was adopted as the membrane material. Methyl methacrylate (MMA),<sup>54</sup> ethyl methacrylate (EMA),<sup>54</sup> propyl methacrylate (PMA),<sup>54</sup> butyl methacrylate (BMA),<sup>54</sup> styrene (ST),<sup>55</sup> potassium persulfate (KPS),<sup>54</sup> and formic acid<sup>55</sup> were purified before use. 2-Butanone [methyl ethyl ketone (MEK)], 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), benzene, and cyclohexane were used without further purification. Distilled water was employed.

### Graft polymerization

An ampule containing prescribed amounts of SELAR, monomer, KPS, and formic acid was degassed with

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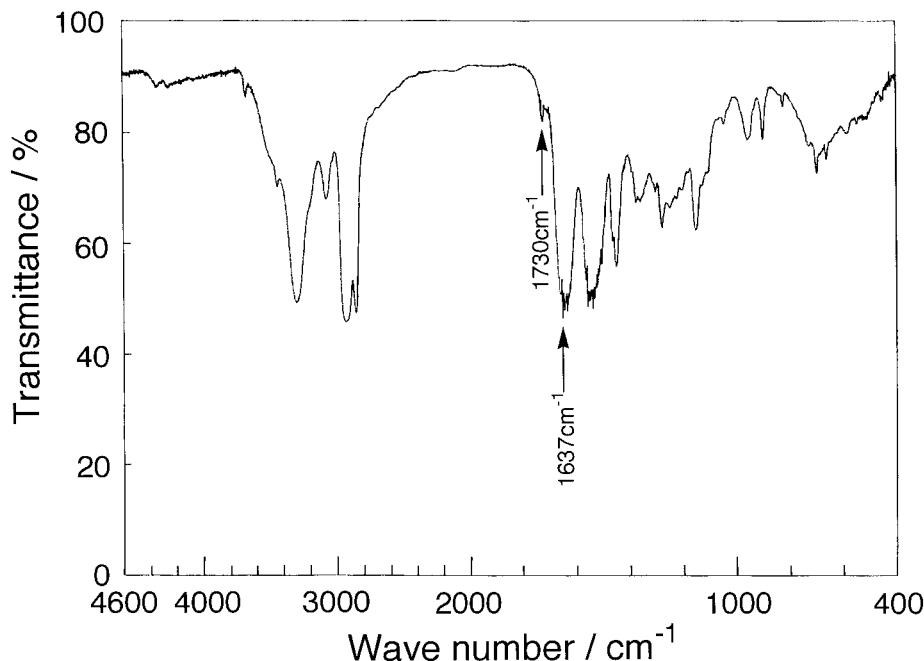


Figure 1 IR spectrum of SEPMMA-038 (PMMA/SELAR = 0.038).

three freeze–pump–thaw cycles and sealed off under a reduced pressure that was below  $10^{-4}$  mmHg. The sealed ampule was shaken in a water bath at a constant temperature of  $80^{\circ}\text{C}$  for 1 h. The reaction mixture was poured into a large amount of nonsolvents of SELAR, such as MEK. The obtained precipitates were filtered and dried at  $50^{\circ}\text{C}$  *in vacuo*.

### Spectroscopic measurements

IR spectra were taken on a Jasco FT/IR-5300 Fourier transform infrared spectrophotometer.

The  $^1\text{H-NMR}$  spectra were obtained with a Varian Gemini 200 NMR spectrometer. The spectra were measured at ambient temperature with a  $100\text{ g dm}^{-3}$  1,1,1,3,3,3-hexafluoro-2-propanol- $d_2$  solution and with tetramethylsilane as the internal standard.

### Preparation of the membranes

The membranes were prepared from an HFIP solution. The HFIP solution, containing 0.50 g of membrane material and  $5.0\text{ cm}^3$  of HFIP, was poured into a Teflon laboratory dish (7.5 cm in diameter), and the solvent was allowed to evaporate at  $25^{\circ}\text{C}$  for 24 h. The obtained membrane was dried *in vacuo* at  $150^{\circ}\text{C}$  for an additional 24 h. The thickness of the obtained membrane was 17–24  $\mu\text{m}$ .

### Pervaporation

The permeation of the benzene/cyclohexane mixture was performed with an ordinary pervaporation tech-

nique.<sup>56</sup> The membrane area in contact with the liquid feed was  $17.3\text{ cm}^2$ . The downstream pressure applied was around 267 Pa (2.0 mmHg). Pervaporation experiments were carried out at a constant temperature of  $50^{\circ}\text{C}$ .

Separation analysis was carried out on a Shimadzu GC-8APT gas chromatograph equipped with a 3.0-m-long column packed with poly(ethylene glycol) 20M [Chromosorb W (AW-DMCS)].

The separation factor,  $\alpha$ , is defined as follows:

$$\alpha = (Y_{\text{benzene}}/Y_{\text{cyclohexane}})/(X_{\text{benzene}}/X_{\text{cyclohexane}})$$

where  $Y_i$  is the weight fraction in the permeate and  $X_i$  is the weight fraction in the feed.

## RESULTS AND DISCUSSION

### Preparation of the membrane materials

The introduction of the monomers onto SELAR was confirmed by IR and  $^1\text{H-NMR}$  spectra of the graft polymers. An example of an IR spectrum is shown in Figure 1. The IR spectrum has a new absorption peak at  $1730\text{ cm}^{-1}$ , which is assigned to the C=O stretching band of poly(methyl methacrylate) (PMMA) and can be detected in addition to the characteristic absorption peak at  $1637\text{ cm}^{-1}$  assigned to the amide I band. The existence of PMMA in SELAR was also confirmed by  $^1\text{H-NMR}$  measurements. The  $^1\text{H-NMR}$  spectrum of SEPMMA-038 is shown in Figure 2. The intensity of the methyl protons (f) in PMMA, which can be observed around 1.3 ppm, and the area of the methylene

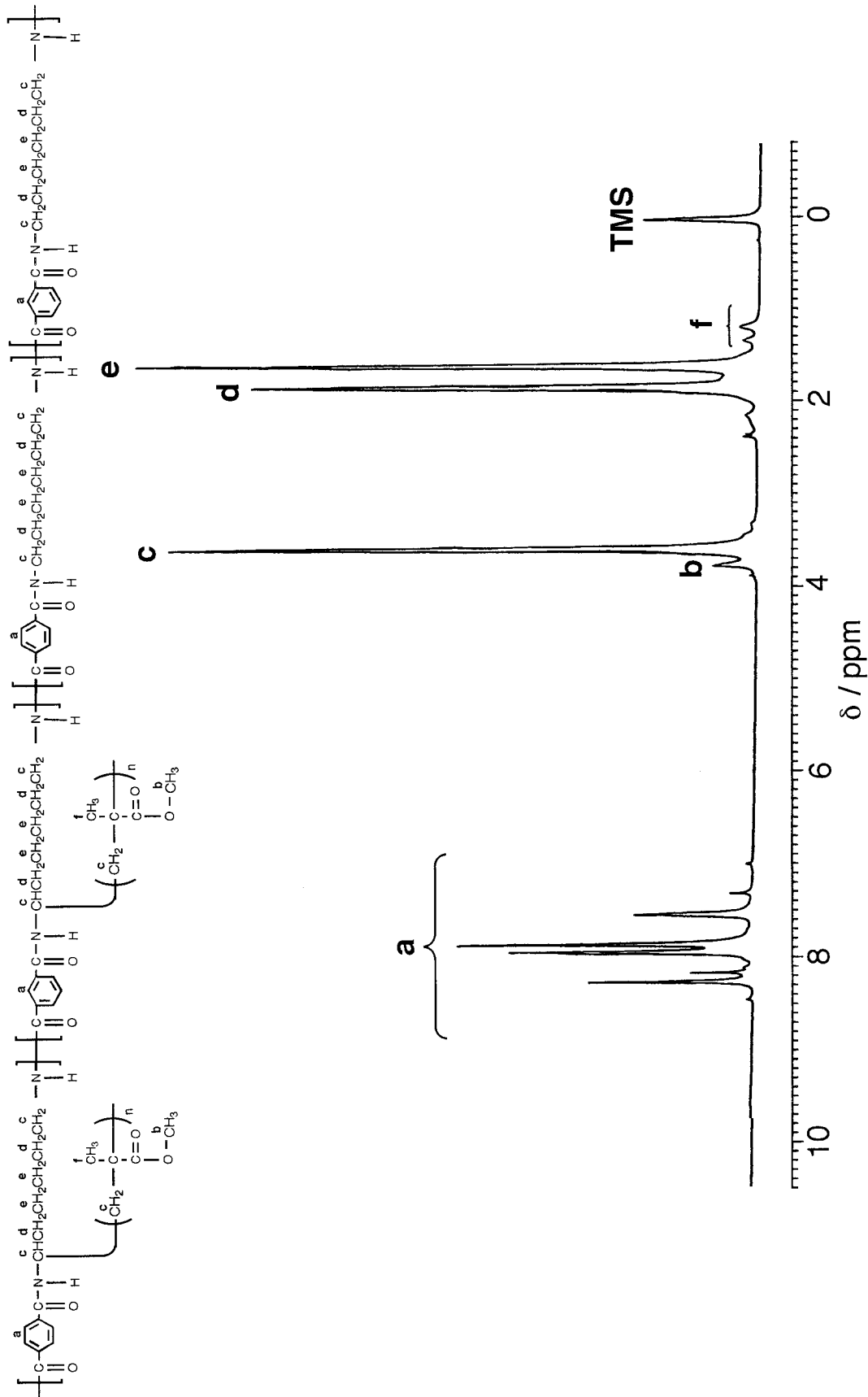


Figure 2 <sup>1</sup>H-NMR spectrum of SEPMMA-038 (PMMA/SELAR = 0.038).

TABLE 1  
Results of Graft Polymerization<sup>a</sup>

Sample	Charged amounts				SELAR-graft-polymer		Polymer fraction	
	SELAR (g)	Monomer (g)	KPS (g)	Monomer/SELAR <sup>b</sup>	Yield (g)	Polymer/SELAR <sup>c</sup>	(wt)	(mol)
SEPMMA-018	2.000	0.813	0.220	1.000	0.582	0.018	0.007	0.018
SEPMMA-029	2.000	1.626	0.220	2.000	1.159	0.029	0.012	0.028
SEPMMA-038	2.000	2.439	0.220	3.000	1.742	0.038	0.015	0.037
SEPMMA-042	2.000	3.252	0.220	4.000	2.310	0.042	0.017	0.040
SEPEMA-008	2.000	0.927	0.220	1.000	0.576	0.008	0.004	0.008
SEPEMA-016	2.000	1.854	0.220	2.000	1.152	0.016	0.007	0.016
SEPEMA-026	2.005	2.787	0.220	3.000	1.641	0.026	0.012	0.025
SEPEMA-030	2.000	3.707	0.220	4.000	2.303	0.030	0.014	0.029
SEPPMA-000	2.000	1.042	0.220	1.000	0.571	0.000	0.000	0.000
SEPPMA-005	2.000	2.084	0.220	2.000	2.005	0.005	0.003	0.005
SEPPMA-008	2.000	3.122	0.220	3.000	1.719	0.008	0.004	0.008
SEPPMA-010	2.000	4.168	0.220	4.000	1.859	0.010	0.005	0.010
SEPBMA-000	2.005	3.469	0.221	3.000	1.693	0.000	0.000	0.000
SEPBMA-000	2.005	3.469	0.441	3.000	2.169	0.000	0.000	0.000
SEPST-009	2.000	0.847	0.220	1.000	0.577	0.009	0.004	0.009
SEPST-016	2.000	1.693	0.220	2.000	1.152	0.016	0.007	0.016
SEPST-038	2.000	2.541	0.220	3.000	1.840	0.038	0.016	0.037
SEPST-070	2.000	3.387	0.220	4.000	2.326	0.070	0.029	0.065

<sup>a</sup> Graft polymerization was carried out at 80°C for 1 h in 40 cm<sup>3</sup> of formic acid.

<sup>b</sup> Ratio of a mole of charged monomer to a unit mole of charged SELAR.

<sup>c</sup> Ratio of a unit mole of polymer grafted to that of SELAR.

protons of SELAR (c, d, and e) led to a PMMA/SELAR ratio of 0.038. Other polymer compositions were also determined with <sup>1</sup>H-NMR spectra. The results of the graft polymerizations are summarized in Table I. In the sample code, the last three numbers show the ratio of a unit mole of the grafted polymer to that of SELAR. Among the four kinds of methacrylate monomers, the longer the alkyl group is of the ester moiety, the smaller the amount is of the polymer grafted onto SELAR. The graft polymerization of BMA onto SELAR was hardly observed under these graft polymerization conditions. Those grafted polymers, except for SEPEMA-008 and SEPPMA-008, gave tough membranes like SELAR did.

### Pervaporation

The pervaporation results for the membranes with different grafted polymers are shown in Figures 3–6, in which the weight fractions of benzene in the permeate are plotted against those in the feed. Vapor-liquid equilibrium curves for benzene/cyclohexane mixtures at 50°C (dashed lines)<sup>57</sup> and diagonal lines (solid lines) are given in all the figures. Unmodified SELAR membranes transported benzene in preference to cyclohexane below the feed fraction range of 0.9. The permselectivity of SELAR is higher than that of nylon 6.<sup>25</sup> This is thought to be due to the fact that SELAR consists of a phenylene moiety, whereas nylon

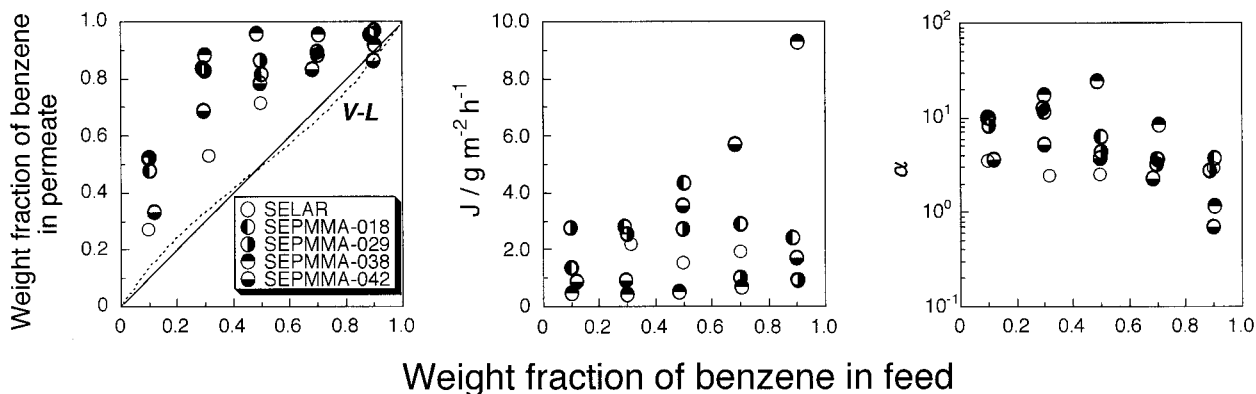
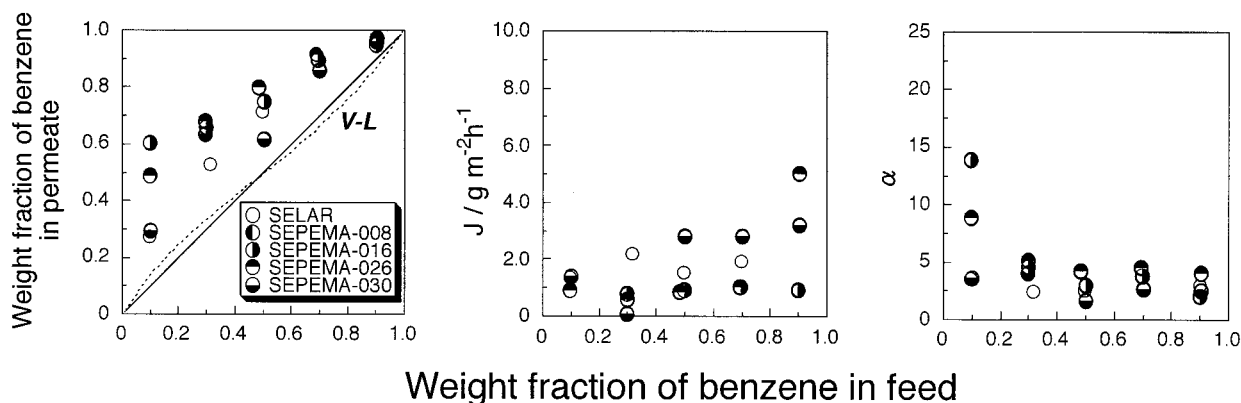


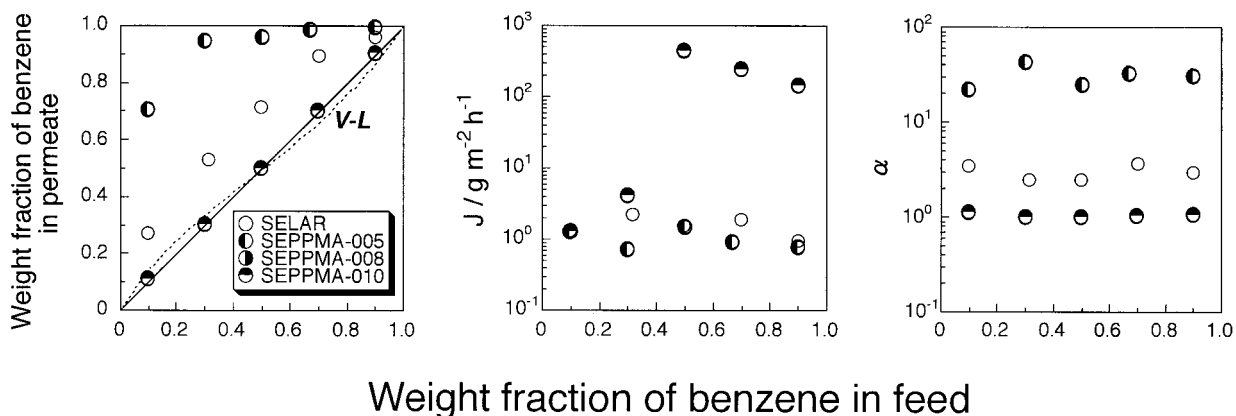
Figure 3 Effect of the feed composition on the separation of benzene/cyclohexane mixtures through SEPMA membranes [operating temperature = 50°C; downstream pressure = 267 Pa (2 mmHg)].



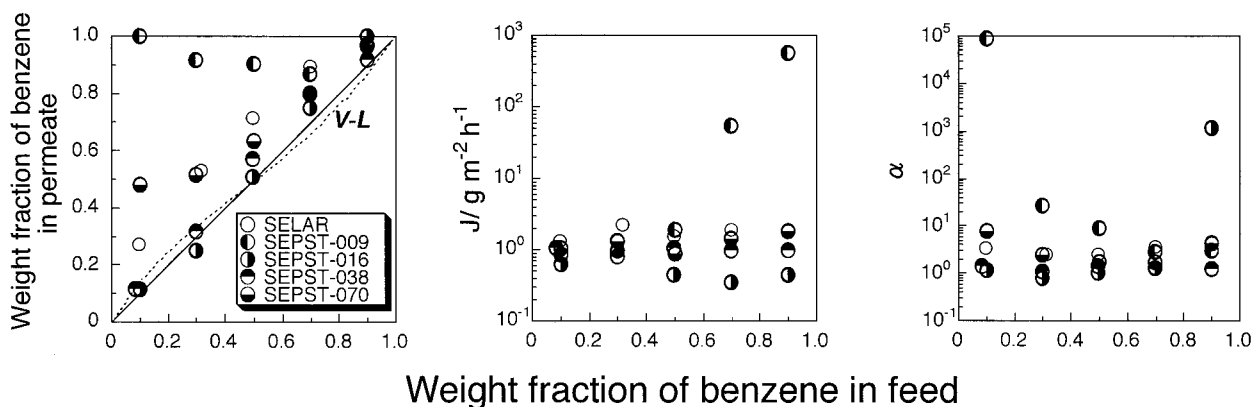
**Figure 4** Effect of the feed composition on the separation of benzene/cyclohexane mixtures through SEPEMA membranes [operating temperature = 50°C; downstream pressure = 267 Pa (2 mmHg)].

6 has a hexamethylene moiety as a dicarboxylic acid component. All membranes from grafted SELAR did not show good membrane performance. The modified SELAR membranes, with suitable graft contents, showed permselectivity toward benzene. In particular, the SEPPMA-005 membrane showed a higher permselectivity than an unmodified SELAR mem-

brane over the whole range of feed fractions, but its flux values were not enhanced. In general, the introduction of a grafted polymer, showing an affinity toward benzene, onto a membrane enhanced the solubility of the target permeant, and the swelling of the membrane by the sorbed target permeant was also induced. This led to the decrease in permselectivity.



**Figure 5** Effect of the feed composition on the separation of benzene/cyclohexane mixtures through SEPPMA membranes [operating temperature = 50°C; downstream pressure = 267 Pa (2 mmHg)].



**Figure 6** Effect of the feed composition on the separation of benzene/cyclohexane mixtures through SEPST membranes [operating temperature = 50°C; downstream pressure = 267 Pa (2 mmHg)].

The selection of a more suitable monomer grafted to a polymer backbone showing an affinity toward benzene and a suitable content of the grafted polymer led to a membrane showing higher membrane performance.

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