

## DIENE-*N*-(2,4,6-TRIBROMOPHENYL)MALEIMIDE COPOLYMER MEMBRANES FOR PERVAPORATION OF ETHANOL-WATER MIXTURES

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Alternating copolymers of butadiene or isoprene with *N*-(2,4,6-tribromophenyl)maleimide and the copolymer of chloroprene containing 42.7 mole % *N*-(2,4,6-tribromophenyl)maleimide structure units were synthesized by radical copolymerization. Along with copolymerization, the Diels-Alder addition of comonomers proceeded. DSC revealed some crosslinking of the copolymers occurring even at room temperature. Homogeneous membranes were prepared from the copolymers by solution casting and tested in pervaporation of variously concentrated aqueous ethanol. Separation factors of the membranes related to the preferentially transported water increased with increasing content of ethanol in solutions to be separated. In contrast to hydrophilic maleimide groups, the incorporated diene units lowered separation efficiency due to their affinity to ethanol.

Copolymers of vinyl monomers with maleimide and its derivatives applied as membrane materials for pervaporation separation of aqueous ethanolic solutions were the subject of several studies<sup>1-5</sup>. Water permeated preferentially through membranes made from them. In contrast to ethanol, in the water transport carbonyl groups in maleimide structure units function as carriers. Both the separation factor and the permeate flux depended on the composition and polarity of a membrane. However, only the copolymers containing less than 20 mole % maleimide units have been investigated so far.

This study concerns pervaporation behaviour of membranes prepared from the alternating copolymers of butadiene (BT) or isoprene (IP) with *N*-(2,4,6-tribromophenyl)-maleimide (TBPM) and from the copolymer of chloroprene (CP) containing 42.7 mole % *N*-(2,4,6-tribromophenyl)maleimide structure units. The aim was to evaluate the influence of a high content of maleimide units in polymer chains on membrane separation properties in pervaporation of ethanol-water mixtures.

## EXPERIMENTAL

### Materials

*N*-(2,4,6-Tribromophenyl)maleimide (m.p. 142 °C) was synthesized by cyclodehydration of the corresponding maleamic acid<sup>6</sup>. Butadiene, isoprene and chloroprene were commercial products. The solvents used were chromatographically pure.

Copolymers of the dienes with *N*-(2,4,6-tribromophenyl)maleimide were prepared by radical copolymerization in dimethylformamide or chloroform at 50 °C using azobis(isobutyronitrile) (AIBN) as an initiator<sup>7</sup>.

### Preparation of Membranes

Membranes with a thickness of ca 30 μm were obtained by casting chloroform solutions (0.1 g l<sup>-1</sup>) of copolymers on a glass plate to form a 0.35 mm layer and by solvent evaporation at room temperature.

### Methods

The glass transition temperatures ( $T_g$ ) of the copolymers were determined by DSC on a Perkin-Elmer DSC 7 apparatus at a heating rate of 10 °C min<sup>-1</sup> and 5 °C min<sup>-1</sup> in nitrogen atmosphere and in air, respectively.

Pervaporation of ethanol-water mixtures was performed as described earlier<sup>4</sup>. Membranes were characterized by the separation factor related to the preferentially transported water and by the permeate flux, i.e. the amount of liquid which is transported through the membrane per unit area and unit time. The separation factor,  $\alpha_{\text{H}_2\text{O}}$ , is defined as

$$\alpha_{\text{H}_2\text{O}} = \frac{w_{\text{H}_2\text{O}}^{\text{P}} w_{\text{EtOH}}^{\text{F}}}{w_{\text{EtOH}}^{\text{P}} w_{\text{H}_2\text{O}}^{\text{F}}}, \quad (1)$$

where  $w^{\text{P}}$  and  $w^{\text{F}}$  are the weight fractions of components in the permeate and in the feed, respectively.

The fluxes of the different membranes were normalized to a membrane thickness of 30 μm assuming the proportionality between the flux and the reciprocal membrane thickness.

The components of the permeate were analyzed by gas chromatography.

## RESULTS AND DISCUSSION

### *Diene-N-(2,4,6-Tribromophenyl)maleimide Copolymers*

Synthesis and some properties of diene-TBPM copolymers were reported in our previous study<sup>7</sup>. In the copolymerization, Diels-Alder adducts of comonomers were formed. They were removed by the reprecipitation of the copolymers. For preparation of pervaporation membranes, the copolymers of composition and limiting viscosity numbers ( $[\eta]$ ) given in Table I were used. Table I shows also characteristics of styrene (ST)-TBPM copolymer, which was synthesized and used as the membrane material in the pervaporation separation of ethanol-water mixtures along with other styrene-sub-

stituted *N*-phenylmaleimide copolymers containing less than 10 mole % maleimide groups<sup>4</sup>.

Press-moulding of the diene copolymers at 250 °C and 9.15 MPa led to brittle sheets<sup>7</sup>, but compact films exhibiting good mechanical resistance in handling were prepared by casting chloroform solutions of the copolymers. The films made of IP-TBPM and CP-TBPM copolymers were tougher than those of BT-TBPM copolymer.

Table II summarizes the  $T_g$  values of the diene-TBPM copolymers, which were found in repeated heating-cooling runs. For comparison,  $T_g$ 's of styrene-*N*-(2,4,6-tribromophenyl)maleimide copolymer are also presented. While for the diene copolymers these values increased in consecutive measurements or even, as in the case of the BT-TBPM copolymer, after keeping at room temperature for a long time,  $T_g$ 's of the ST-TBPM copolymer varied only slightly.

An increase in  $T_g$ 's indicated that crosslinking took place. Obviously, polymer radicals are easily formed from diene copolymers with participation of polymer hydroper-

TABLE I

Composition and limiting viscosity numbers of diene-TBPM and styrene-TBPM copolymers

Copolymer	TBPM unit, mole %	$[\eta]^a$ , ml g <sup>-1</sup>	Reference
BT-TBPM	49.7	30.0	7
IP-TBPM	50.3	41.3	7
CP-TBPM	42.7	43.0	7
ST-TBPM	4.1	83.0 <sup>b</sup>	4

BT butadiene; IP isoprene; CP chloroprene; TBPM *N*-(2,4,6-tribromophenyl)maleimide. <sup>a</sup> In tetrahydrofuran at 20 °C; <sup>b</sup> in benzene at 20 °C.

TABLE II

$T_g$  values of diene or styrene-TBPM copolymers

Copolymer	$T_g^a$ , °C			
	1	2	3	4
BT-TBPM	78.5 (94.4) <sup>b</sup>	106.5	119.4	121.6
IP-TBPM	87.3	120.5	132.6	134.1
CP-TBPM	69.8	88.4	102.6	—
ST-TBPM	116.5	114.3	114.6	112.8

<sup>a</sup> Obtained in the 1st – 3rd scan under nitrogen, in the 4th scan in air; <sup>b</sup> after 11 months at room temperature.

oxides. The polymer radicals can combine forming a crosslinked polymer structure with limited mobility of polymer chains and, consequently, with a higher  $T_g$  value. In the fourth run carried out in air, the increase in  $T_g$ 's was only small. It appears that the possibility of further crosslinking and hence a  $T_g$  increase are reduced with the increasing number of crosslinks.

An attempt to prepare mechanically resistant sheets by press-moulding of diene-TBPM copolymers was obviously unsuccessful because the crosslinking reactions occurred during processing. As a result, brittle materials were formed.

*Pervaporation of EtOH-H<sub>2</sub>O Mixtures through Diene-N-(2,4,6-Tribromophenyl)-maleimide Copolymer Membranes*

In the pervaporation of variously concentrated ethanol-water mixtures, the membranes showed increasing separation factors related to the preferentially transported water, as the content of ethanol in the feed increased (Table III). A similar trend was observed with styrene-substituted *N*-phenylmaleimide copolymer membranes<sup>4</sup>. The maximum value (25.6 at 87.1% EtOH in the feed) was reached using the IP-TBPM copolymer membrane. The permeate fluxes were 10 g m<sup>-2</sup> h<sup>-1</sup> and 5 g m<sup>-2</sup> h<sup>-1</sup> for the BT-TBPM or IP-TBPM and CP-TBPM copolymer membranes, respectively. The higher separation factors and permeate fluxes of the membranes made of the alternating copolymers than those obtained for the CP-TBPM copolymer membrane can be due to their greater maleimide contents. However, as found previously<sup>4</sup>, styrene-substituted *N*-phenyl-

TABLE III  
Pervaporation of EtOH-H<sub>2</sub>O mixtures through diene-TBPM copolymer membranes at 35°C

Copolymer	EtOH content, wt. %		Separation factor
	feed	permeate	
BT-TBPM	59.9	12.0	11.0
	78.0	16.2	18.3
IP-TBPM	44.6	10.0	7.6
	59.7	8.4	16.2
	70.4	11.1	19.1
	72.0	10.3	22.5
	85.8	19.6	24.9
CP-TBPM	87.1	20.8	25.6
	61.4	15.6	8.6
	78.3	22.3	12.6
	85.7	21.4	21.9

maleimide copolymer membranes with less than 10 mole % maleimide units showed separation factors up to 2.5 times higher than the diene alternating copolymer membranes, and comparable permeate fluxes. This documents that diene units in the polymer chain considerably influence resulting pervaporation properties. In contrast to carbonyl groups in maleimide units, which are carriers for water, the incorporated dienes facilitate sorption and diffusion of ethanol<sup>8</sup>. As constituents of the glassy copolymer, dienes are operative to a smaller extent than they could be in elastomer chains. Hence, while the glassy state and a high maleimide content are favourable for the water transport, the incorporated diene units lower separation efficiency towards water.

### CONCLUSION

Membranes made of copolymers of butadiene, isoprene and chloroprene with *N*-(2,4,6-tribromophenyl)maleimide containing 49.7, 50.3, and 42.7 mole % maleimide units, respectively, transport preferentially water in pervaporation of aqueous ethanolic solutions. Their separation efficiency increases with increasing content of ethanol in the mixture to be separated. A favourable influence of maleimide groups on the water transport is impaired by diene units showing higher affinity towards ethanol.

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