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Note

Preliminary results on the gas chromatographic evaluation of interpenetrating polymer networks prepared from porous polymer beads

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Chemical modification of the column packing is an attractive way to change the gas chromatographic (GC) performance of a stationary phase. This approach is still under intensive investigation even for such common materials as porous polymers. However, commercially available porous polymers often exhibit very inhomogeneous physical and chemical structures. Recent improvements in the synthesis of highly cross-linked porous polymers have led to their use as a reversed-phase liquid chromatographic packing materials. Nevertheless, efforts have been made to limit their swelling in organic solvents and to make them more water compatible. It has been reported that chemical derivatization of polystyrene beads obtained by introducing ether linkages into the polystyrene backbone makes them more suitable for the separation of biomolecules in aqueous solution[1].

This paper proposes a novel chemical derivatization technique as a means of changing the chromatographic behaviour of some porous polymer packings by producing a structure defined as an interpenetrating polymer network. This kind of derivatization may also be helpful for changing the hydrophobic properties of polymer packings and for reducing their swelling inorganic solvents.

In general, an interpenetrating polymer network is a material containing at least two polymers, each in a network form. When a cross-linked polymer I, swollen with a monomer II, is subjected to polymerization, it results in a sequential interpenetrating polymer network (IPN)[2]. A full IPN is obtained when both components are cross-linked (thermosetting polymers). If one is a linear polymer and the other is in the network form, the system is called a semi-IPN. From the point of view of such definitions, some ion-exchange resins, called "snake-cages", can be regarded as a type of sequential IPN, especially when the "snakes", *i.e.*, linear polyelectrolytes, are cross-linked[3].

Recently, sequential IPNs of both types have been prepared on the basis of porous bead copolymers, made of methyl methacrylate (MMA) and di(methacryloyloxymethyl)naphthalene (DMN), by swelling them with monomers and then by *in situ* polymerization[4–6]. Full IPNs have been prepared with the aim of increasing their surface area and pore volume without weakening the physical strength of the

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starting material. Usually full IPNs exhibit high densities, less swelling in organic solvents and substantial changes in specific surface area, pore size distribution and pore volume, which depend mainly on the type of monomer II used and the porous structure of the starting copolymers. For these reasons, full IPNs seem to be especially suitable for GC.

In this work, IPN-modified MMA–DMN copolymers were tested as column packings in GC and attempts were made to correlate their chromatographic behaviour with the conditions of IPN synthesis.

EXPERIMENTAL

Materials

The bead polymer sorbents used as network I in the IPN syntheses were porous bead MMA–DMN copolymers prepared under different conditions via radical suspension copolymerization of methyl methacrylate with DMN in the presence of toluene and isooctane or toluene and dodecane as diluents and 2,2'-azobisisobutyronitrile as initiator[7–9]. The characterization of these materials and their synthesis conditions are given in Table I.

TABLE I

CHARACTERIZATION OF MMA–DMN COPOLYMERS USED FOR IPN SYNTHESES

Copolymer No.	*DMN content (%, w/w)*	*Specific surface area (m^2/g)*	*Specific pore volume (cm^3/g)*	*True density (g/cm^3)*	*Pore-size distribution (Å)*	*Type*
1	50	0.1	–	1.40	–	Gel
2	50	44.3	0.40	1.42	10–243	Porous
3	50	63.8	0.25	1.42	10–730	Macroporous
4	60	124.0	0.53	1.45	10–6000	Macroporous

IPN preparation

MMA–DMN copolymer beads were swollen in a swelling agent consisting of a monomer (or monomer mixture), an initiator and a solvent. In some instances pore-forming diluents (toluene and dodecane) were used to replace the solvent. The amount of swelling agent used was such that it was completely absorbed by the polymer. After 24 h of swelling, the excess was removed by aspiration. The swollen beads were placed in an aqueous solution of poly(vinyl alcohol) (2%, w/w) at 80°C for 10 h. The beads were then washed with hot water and sequentially in a Soxhlet apparatus with acetone and then methanol.

Mixtures of MMA and DMN, ethylene glycol dimethacrylate (EGDMA) or solutions of DMN in toluene were used as monomer II. Details of the synthesis are given in Table II.

Measurements

Specific surface area, specific pore volume and pore size distributions were obtained by using BET and Barret methods. The apparatus used was a Sorptomatic 1800 (Carlo Erba, Milan, Italy).

Chromatographic measurements were carried out on a Chromatron GCHF-18.3 gas chromatograph (Chromatron, Berlin, G.D.R.) equipped with a flame ionization or thermal conductivity detector. Modified copolymer beads were packed in a glass column (1 m × 2.5 mm I.D.). Samples of 0.2 μl of test mixtures were injected; the concentration of any alcohol in the test mixture was 0.1% (v/v) and that of any alkane was 0.16% (v/v).

RESULTS AND DISCUSSION

The MMA–DMN copolymer used for the preparation of IPNs had three different porous structure: (a) gel-type structure with an unmeasurable surface area and an unmeasurable pore volume; they are recognized as empty beads of extremely low apparent density[8]; (b) porous structure with a moderately developed surface, intermediate pore sizes ($r \leqslant 400$ Å) and low pore volume; (c) macroporous structure with a well developed surface, measurable macropores and large pore volume.

These copolymers were subjected to post-polymerization according to the following procedures:

(i) Formation of a porous network II within a gel-type structure. The swelling medium consisted of a monomer mixture containing cross-linking monomer (MMA + DMN), an initiator and a pore-forming diluent (toluene + dodecane) (samples 1a and c, Table II).

(ii) Formation of a network II inside the macroporous copolymer by swelling it with liquid cross-linking monomer (EGDMA) containing an initiator (sample 2, Table II).

(iii) Formation of a network II within gel-type (empty) beads by swelling them with the liquid monomer (EGDMA) containing an initiator (sample 1b, Table II).

(iv) Formation of a porous network II inside the copolymer of developed porous structure (porous or macroporous type). The monomer mixture containing the cross-linker (DMN) and pore-forming diluent was used as a swelling medium (samples 3 and 4b, Table II).

(v) Formation of a network II within the copolymer of well developed porous structure. Cross-linking monomer (DMN) diluted with solvent and containing an initiator was used as a swelling medium (sample 4a, Table II).

All the IPNs prepared were subjected GC tests. The results obtained indicate that their chromatographic behaviour is different from that of parent copolymer (Table III).

IPNs based on copolymer I were characterized by the appearance of a certain porosity resulting in a measurable surface area and broad pore-size distribution. The results indicate that copolymer I increases its surface area after post-polymerization with or without a pore-forming diluent (first and third type of IPN procedures, samples 1a, b and c, Table II). However, this increase is insufficient to result in satisfactory efficiency of the column (Table III).

The second type of IPN synthesis, based on a macroporous copolymer, also exhibited a worse column performance in comparison with the starting copolymer (sample 2, Tables II and III).

In the fourth type of IPN synthesis, based on macroporous copolymers, the modified copolymers always exhibited a reduction in surface area and pore volume

TABLE II

EXPERIMENTAL DETAILS OF IPN SYNTHESES BASED ON MMA-DMN COPOLYMERS

Sample code	*Starting copolymer*	*Swelling mixture (w/w)*	*Specific surface area (m^2/g)*	*Specific pore volume (cm^3/g)*	*$d/2$[a] (Å)*	*True density (g/cm^3)*	*Description*
1a	Copolymer 1	MMA–DMN (1:1) in toluene–isooctane (4:1)	Unmeasurable	–	–	1.50	White, fragile beads with surface irregularities
1b	Copolymer 1	EGDMA	36.0	–	10–2120	1.52	White, strong, regular beads
1c	Copolymer 1	MMA–DMN (2:3) in toluene–dodecane (9:2)	40.1	1.32	10–2120	1.50	White, fragile beads with surface irregularities
2	Copolymer 2	EGDMA	43.0	1.21	10–2230	1.52	White, strong, regular beads
3	Copolymer 3	MMA–DMN (2:3) in toluene–dodecane (7:1)	30.6	0.74	10–830	1.49	White, regular beads like copolymer 3
4a	Copolymer 4	DMN in toluene (1:5)	85.0	0.49	10–500	1.55	White, regular beads like copolymer 4
4b	Copolymer 4	DMN in toluene–isooctane (4:1)	25.7	0.21	10–240	1.50	White beads with surface irregularities

[a] $d/2$ = Pore-size distribution.

TABLE III

COMPARISON OF MMA–DMN COPOLYMERS AND THEIR IPN DERIVATIVES

Column packing	*Theoretical plates for*		R_{ij}[a]	*Separation of alcohols*[b]	*Separation of n-alkanes*[c]	*Separation conditions*
	Propanol	*Heptane*				
Copolymer 1	20	10	–	No resolution	No resolution	Studied temperature range 100–200°C at flow-rate 30 ml/min
IPN 1a	62	30	–	3 peaks weakly separated	No resolution	Temp. 140°C; flow-rate 30 ml/min; time of alcohol analysis, 4.5 min
IPN 1b	50	30	–	No resolution	No resolution	Temp. 100–200°C; flow-rate 30 ml/min
IPN 1c	180	60	–	Partial resolution (3 peaks)	Partial resolution (2 peaks)	Temp. 140°C; flow-rate 30 ml/min; time of alcohol analysis, 3.5 min; time of alkane analysis, 2 min
Copolymer 2	415	110	0.35	Partial resolution (4 peaks)	Partial resolution (4 peaks)	Temp. 160°C; time for alcohol analysis, 3.5 min; time for alkane analysis, 3 min
IPN 2	150	65	–	Partial resolution (7 peaks)	Partial resolution (3 peaks)	Temp. 160°C; flow-rate, 30 ml/min; time for alcohol analysis, 6 min; time for alkane analysis, 5.3 min
Copolymer 3	360	125	0.47	10 peaks weakly separated	Partial resolution (4 peaks)	Temp. 160°C; flow-rate, 30 ml/min; time for alcohol analysis, 8.3 min; time for alkane analysis, 4 min
IPN 3	270	70	0.25	Partial resolution (7 peaks)	Partial resolution (4 peaks)	Temp. 170°C; flow-rate, 30 ml/min; time for alcohol analysis, 10 min; time for alkane analysis, 11 min
Copolymer 4	620	300	0.66	Full resolution	Full resolution	Temp. 175°C; flow-rate, 30 ml/min; time for alcohol analysis, 18.5 min; time for alkane analysis, 15 min at 195°C
IPN 4a	750	340	0.89	Full resolution	Full resolution	Flow-rate, 30 ml/min. Alcohols: temp. 175°C, 6 min. Alkanes: temp. 195°C; time, 11.5 min
IPN 4b	350	130	0.32	10 weakly separated peaks	Partial resolution (5 peaks)	Flow-rate, 30 ml/min. Alcohols: temp. 175°C; time, 18 min. Alkanes: temp. 195°C; time, 11.5 min

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[a] R_{ij} = resolution for the pair of isomers 2-butanol and 2-methylpropanol. $R_{ij} = 2\,t_R(w_{p,i} + w_{p,j})$, where $t_R = t_{Rj} - t_{Ri}$, the distance between the maxima of the two peaks, and $w_{p,i}$ and $w_{p,j}$ are the widths of the peaks determined by extrapolating the points of inflection of the peaks towards the baseline.

[b] Test mixture of alcohols: methanol, ethanol, 1-propanol, 2-propanol, 2-butanol, 2-mehylpropanol, 1-butanol, 2-pentanol, 3-pentanol and 1-pentanol.

[c] Test mixture: C_5–C_{10} *n*-alkanes.

coupled with changes (usually broadening) of the pore-size distribution (samples 3 and 4b, Table II). Such a modification (interpenetration of two porous networks) resulted in a more heterogeneous pore structure with a reduction in the number of theoretical plates and the separation capability of the column (Table III).

The most promising results were obtained with the fifth type of IPN synthesis, where the swelling medium was a toluene solution of a cross-linking monomer, DMN (sample 4a, Table II). Regardless of the decrease in surface area and pore volume, there was a standardization of pore sizes combined with a lowering of the retention times and enhanced column efficiency (Table III, Figs. 1–3). Similar effects have been reported previously by Woeller and Pollock[10], who used incompletely cured styrene–divinylbenzene copolymers. They were swollen with a toluene solution of divinylbenzene and subjected to further polymerization. Such a two-stage bead preparation resulted in high performance and shortening of retention times of test mixtures was observed. Although no information about the actual structure was given, the method of modification indicates that synthesis giving rise to an interpenetrating polymer network was achieved.

The shortening of the retention times observed for IPN 4a might be a consequence of a decrease in specific surface area and its more uniform pore size distribution (Fig. 1). The higher performances observed with this copolymer might be explained by the more uniform structure expected as a result of cross-linking of the strongly inhomogeneous porous polymer network. Post-polymerization of such a system, built from more or less cross-linked units ("hard" and "soft" sites), must result in some level of interpenetration of the two-component network, *i.e.*, at least "soft" sites cross-linked by DMN[2,11,12].

Such interpenetration, for IPNs based on MMA–DMN copolymer, has been confirmed previously in studies of their glass temperatures and chromatographic behaviour[5]. Examination by scanning electron microscopy (SEM) of some selected IPNs based on MMA–DMN copolymers has been reported[5,6]. The SEM studies of

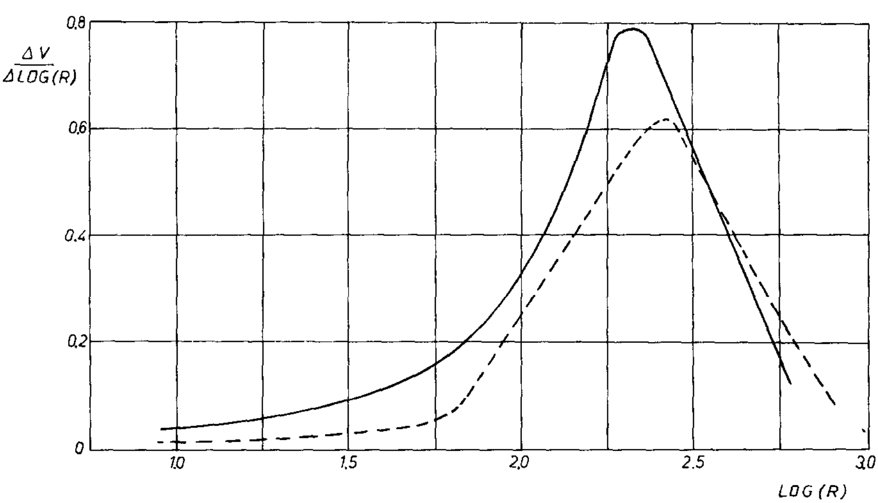

Fig. 1. Pore-size distribution for copolymer 4 (solid line) and IPN 4a (dashed line).

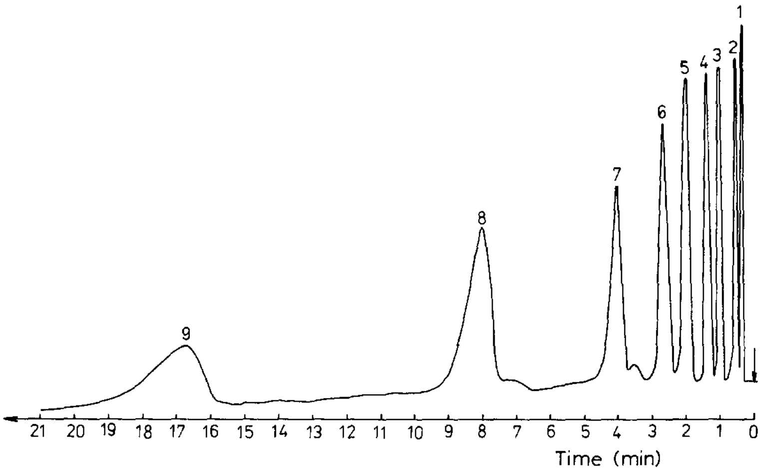

Fig. 2. Separation of alcohols using IPN 4a as a column packing: column, 1 m × 2.5 mm I.D.; temperature, 175°C; flame ionization detector; sample, 0.2 μl; hydrogen flow-rate, 30 ml/min; injector temperature, 200°C; sensitivity, $2 \cdot 10^{-10}$ a.u.f.s. Peaks: 1 = methanol; 2 = ethanol; 3 = *n*-propanol; 4 = *sec.*-butanol; 5 = *n*-butanol; 6 = *n*-pentanol; 7 = *n*-hexanol; 8 = *n*-heptanol; 9 = *n*-octanol.

sample 4a revealed impregnation of the surface copolymer shell (Fig. 4) similar to that observed previously for IPNs. This confirms some interpenetration of the two-component network for this copolymer.

To summarize, modification by formation of a porous network inside the porous copolymer proved not to be promising for GC purposes. This may be explained by an

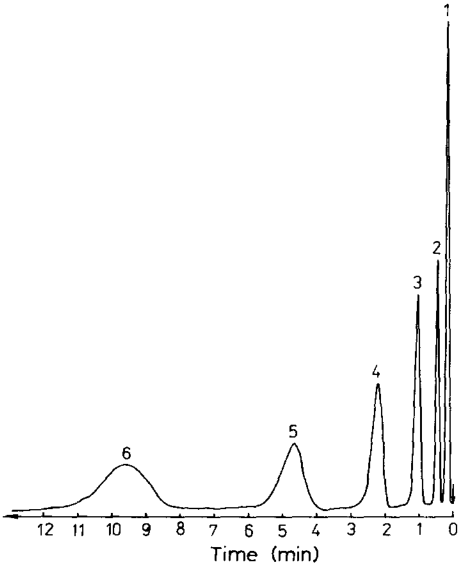

Fig. 3. Separation of *n*-alkanes. Thermal conductivity detector; other conditions as in Fig. 2. Peaks: 1 = pentane; 2 = hexane; 3 = heptane; 4 = octane; 5 = nonane; 6 = decane.

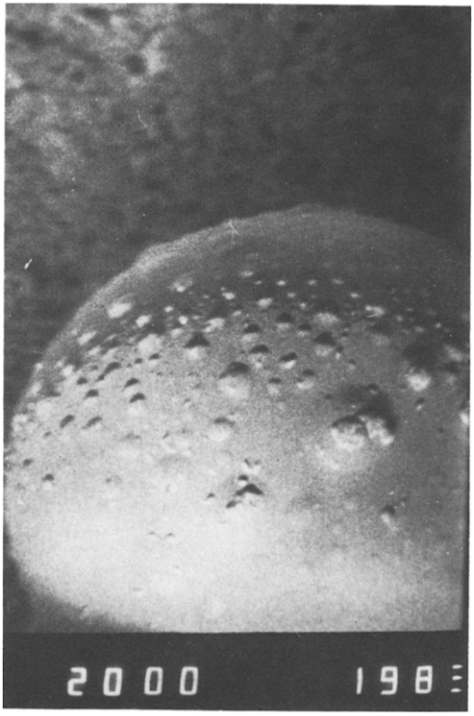

Fig. 4. SEM photograph of sample IPN 4a. Magnification ×2000.

increase in heterogeneity of the system due to post-polymerization. Post-polymerization of copolymers swollen with diluted cross-linking monomer, leading to the formation of a non-porous network interpenetrated with a porous network of the starting copolymer, seems to result in a decrease in the heterogeneity of the system. This may be useful for such purposes as shortening analysis times and improving the column performance.

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