Porous Bead Aliphatic–Aromatic Methacrylate Copolymers. VII. TG, DTA, DSC, and Inverse Gas Chromatography Studies

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Synopsis

The thermal behavior of porous bead methyl methacrylate–di(methacryloyloxymethyl)naphthalene (DMN) copolymers was investigated by TG, DTA, and DSC measurements as well as the inverse gas chromatography method using several different molecular probes. TG and DTA results proved copolymer stability up to 250°C. The retention diagrams for all probes used showed the temperature transitions among which one corresponds to glassy transition of amorphous PMMA. The other features observed on the retention diagrams correspond to a segmental mobility of weakly crosslinked copolymer parts.

INTRODUCTION

The use of gas chromatography to characterize the properties of stationary phases by studying their interaction with volatile solutes is known as inverse gas chromatography. Recently inverse gas chromatography was used to elucidate certain structural features of polymeric materials. The method is usually referred to as the molecular probe technique. From the retention behavior of various low molecular weight probes it was possible to determine such polymer properties as temperature of glass transition, solution thermodynamics, diffusion coefficients, crystallinity, etc. In the case of glassy transition of polymers deposited on inert porous support, instead of the normal linear variation of the logarithm of the retention volume vs. the reciprocal absolute temperature a z-shaped retention diagram was recorded.[1] The temperature of the first deviation from linearity was identified as glass transition temperature. The situation is not clear for the highly crosslinked polymers used as sorbents in gas chromatography. For ethylene glycol dimethacrylate–glycidyl methacrylate macroporous copolymers it was reported that neither DSC nor DTA methods gave the desired response.[2] Studies of macroporous styrene–divinylbenzene copolymers also revealed the deviation from linearity of the retention diagram, although not so significant as in the case of linear polymers.[2] Moreover, the size of the probe and its thermodynamic quality seem to be important in detection of transitions of polymeric sorbents and the retention diagram provides information about the structural properties on the molecular level.[3,4]

In this paper the thermal behavior of macroporous copolymers of methyl methacrylate and di(methacryloyloxymethyl)naphthalene are examined by means of TG, DTA, DSC, and the molecular probe method using probes of different solvent quality.

Recently these bead shaped copolymers have been used as sorbents in gas chromatography.[5] The results obtained are considered with respect to structural properties of the copolymers. Additionally, the influence of the probe concentration in the carrier gas on the retention behavior of the copolymers tested is discussed.

EXPERIMENTAL

Materials

Three porous MMA–DMN copolymers, differing in crosslinking density were selected for experiments. Their preparation procedure was described in detail previously.[6,7] Characterization of these copolymers is given in Table I.

Methods

Calorimetry measurements were carried out on a Perkin-Elmer DSC-1 B apparatus at heating rates of 16, 32, and 64°C/min and cooling rate 4°C/min at sensitivity (mcal/s). The value of T_g, established only for one sample, was taken as the point when the trace departs from linearity.

Simultaneous thermogravimetry (TG) and differential thermal analysis (DTA) measurements were carried out using a Q 1500 D Budapest (Hungary) derivatograph with heating rate of 5°C/min in air.

The chromatographic measurements were carried out on a Chromatron GCHF–18.3 gas chromatograph (Chromatron, Berlin, GDR) equipped with a thermal conductivity detector. The carrier gas was helium. The glass columns used were of diameter 2.5 mm and 1 m long. A grain fraction of 0.15–0.2 mm was used.

The specific retention volume V_g was calculated from chromatographic data by means of the equation:

$$V_g = \frac{j \times F \times 273.15}{w \cdot T}(t - t_0)$$

where t and t_0 are retention times for the probe and the reference (air) peak maxima, respectively, F is gas flow rate at T, j is the factor which corrects for gas compressibility, and w is the weight of copolymer in the column.

The variation of V_g of the probes used with h—the height of the chromatographic peak (as a measure of the probe concentration)—was carried out at

TABLE I
Characterization of MMA–DMN Copolymers Used for Experiments

Sample no.	DMN content in monomer mixture (wt %)	Composition of diluent (% v/v) isooctane–toluene	Specific surface area (m^2/g)
1	50	12.5–87.5	40.6
2	60	16.6–83.4	82.0
3	66.7	16.6–83.4	71.2

several temperatures. Water methanol, acetone, benzene, cyclohexane, and hexane were used as the probes.

RESULTS AND DISCUSSION

T_g and DTA curves obtained for the studied copolymers (Fig. 1) revealed that they are stable up to 250°C and the initial decomposition temperature increases slightly with an increase of crosslink density of copolymers. The low-temperature endothermic minimum at about 85°C observed on DTA curves for copolymers 1–3 and accompanied by small copolymer weight loss has contributed to desorption of physically absorbed water, which is confirmed by the gradual disappearance of the peak after heating for 2 and 4 h at 120°C (Fig. 1). The first exothermic maximum on DTA is most probably due
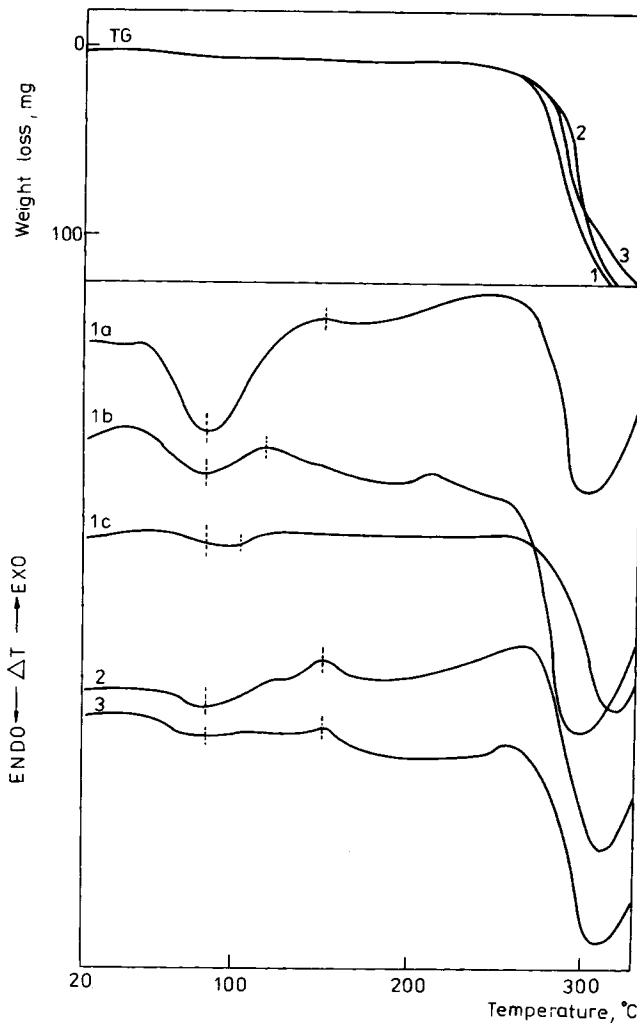

Fig. 1.   TG and DTA curves for copolymers 1–3: (a) sample 1 without heating before DTA test; (b) sample 1 heated at 120°C for 2 h before DTA test; (c) sample 1 heated at 120°C for 4 h before DTA test.

to the disappearance of the unreacted double bonds present in the copolymer structure as a consequence of incomplete crosslinking agent polymerization (see that sample 1c after heating for 4 h before the DTA test does not exhibit this exothermic effect).

The main endothermic effect observed at the temperatures higher than the initial decomposition temperature is due to thermooxidative degradation of the copolymers.[8]

Attempts to determine T_g of MMA–DMN copolymers by DSC failed for samples 2 and 3 and for sample 1 of the lowest crosslink density; DSC gave a slight response which might indicate the glassy transition at 104°C.

To study the variation of V_g with temperature, several probes differing in molecular size and thermodynamic quality were selected. They were solvents and nonsolvents for the polymer under investigation. The range of the temperature was 90–180°C when water, ethanol, and acetone were solutes and 140–180°C when benzene, hexane, and cyclohexane were the solutes since the determination of the retention times of the latter substances was difficult with sufficient accuracy at lower temperatures. Before determination of retention diagram, the changes of V_g with the size of injected probes, expressed by the height of the chromatographic peak were studied to establish the extrapolation of V_g values to zero probe concentration. The variation of V_g with h at three different temperatures for three probes are shown in Figures 2–4.

It was reported that accuracy of T_g detection by means of the molecular probe method is dependent on the concentration of the probe in the carrier gas, especially when the probe is a good solvent and the range of the probe concentration, in which the retention data become independent of h (plateau
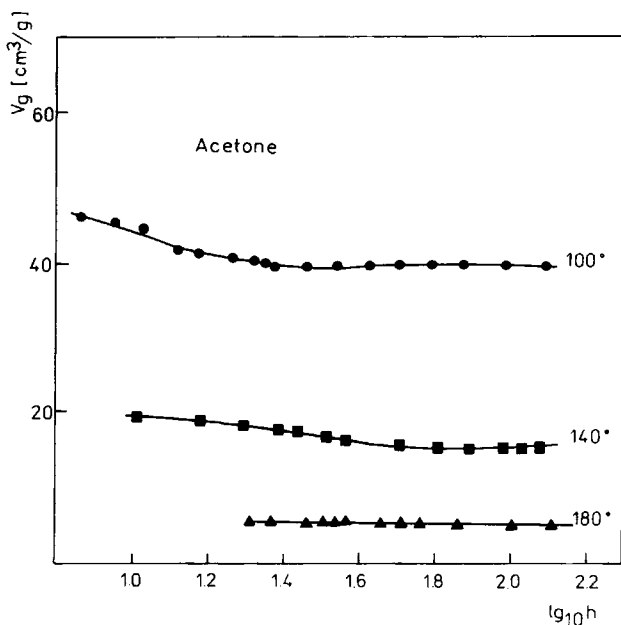

Fig. 2. Specific retention volume of acetone as a function of probe concentration at three different temperatures, 100, 140, and 180°C.
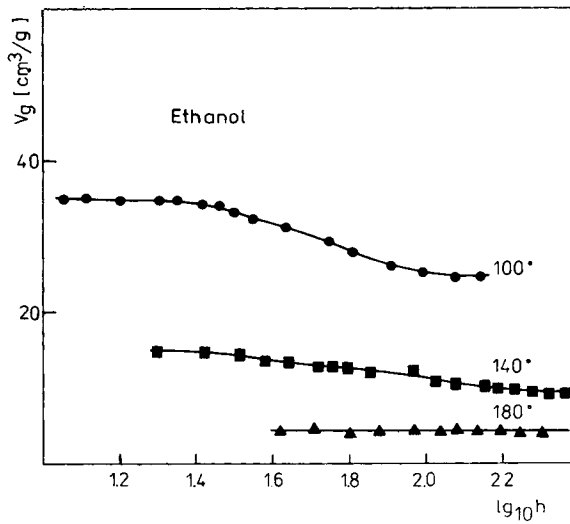
Fig. 3. Specific retention volume of ethanol as a function of probe concentration at three different temperatures, 100, 140, and 180°C.

on the curve V_g vs. log h,[3] should be chosen to establish the retention diagram. However, it appears, from the results presented here, that it is more convenient to use the V_g values extrapolated to zero probe size, since

—a plateau lies usually at the high probe concentration and it is really dangerous to operate beyond the linearity range of the detector

—high probe concentration may exceed the chromatographic column capacity and thus cause disturbances in the retention times.
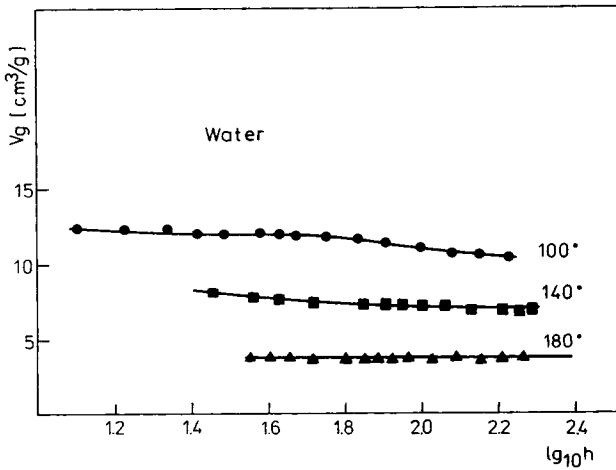

Fig. 4. Specific retention volume of water as a function of probe concentration at three different temperatures 100, 140, and 180°C.

The retention diagrams obtained with water, ethanol, and acetone are presented in Figure 5. The values represented as ordinates are V_g's extrapolated to zero probe size. As suggested by the shape of the logarithmic dependence of retention volumes on reciprocal temperature, the probes used provide a clear evidence of a change in the copolymer surface properties with temperature. The departures from linearity are reproducible for all solutes used in the same manner. First, a clear z-shaped inflection occurs at 104°C, which corresponds to the T_g of amorphous polymethyl methacrylate. Changes in linearity of lower intensity appear above 130 and 150°C, respectively.

The retention diagram of water shows the greatest deviations but it should be emphasized that this molecule is the smallest and as such the most unsuitable for the detection of conformational changes of the copolymer. Furthermore, retention times of water, due to their shortness, are mostly incorrect.

It is generally accepted that glassy transition represents large-scale conformational changes on the molecular level and is a unique and most important parameter characterizing the mechanical behavior of any amorphous polymer. Besides that, and depending on the observation method and definition, the glass transition temperature T_g is also a function of numerous molecular variables, including chemical composition, crosslinking and diluent. Porous polymers in particular represent an inhomogeneous system in which chemical composition and concentration of network junctions (depending upon the change of conditions of heterogeneous crosslinking polymerization during polymerization process) vary through the polymer bead. In particular, styrene–divinylbenzene copolymers, due to the higher reactivity of divinyl-
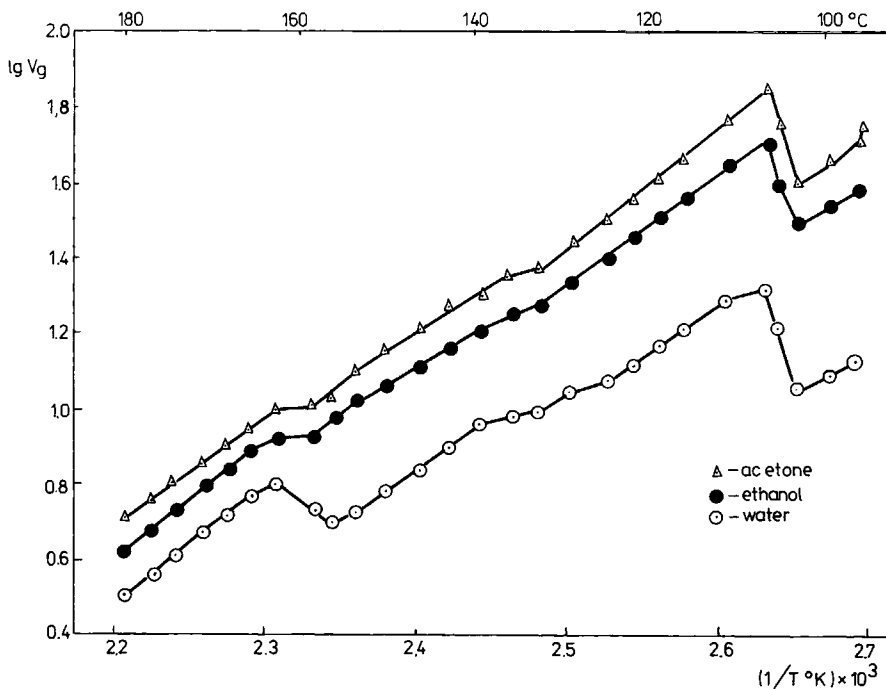

Fig. 5.   Retention diagram for acetone, ethanol, and water on MMA–DMN copolymer 1.
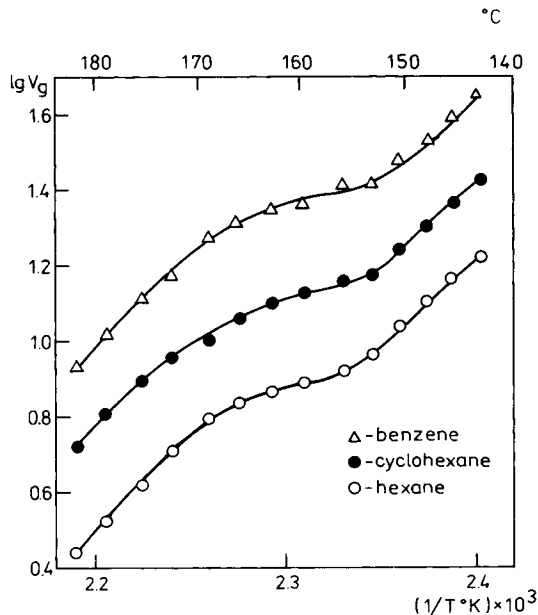
Fig. 6. Retention diagram for benzene, cyclohexane, and hexane on MMA–DMN copolymer 1.

benzene which is consumed more rapidly than styrene, exhibit gradient in copolymer density. This gradient, caused by chemical composition gradient, also causes the number of crosslinking sites to decrease substantially when going from the bead center to the surface. The same may be expected for MMA–DMN copolymer where DMN is a methacrylate analogue of the DVB molecule. As a consequence of these different reactivities at the final stages of copolymerization, longer monomer sequences of MMA occur, or, in particular, MMA polymer chains have been grafted to the copolymer network.

This may be a reason for the strong departure on retention diagrams in the vicinity of the glass transition of PMMA. The same effect was observed for styrene–divinylbenzene copolymers and for acrylonitrile–divinylbenzene copolymers at the T_g of amorphous polystyrene and polyacrylonitrile, respectively.[9, 10]

The transitions observed in the range of 130–150°C (Figs. 5 and 6) probably correspond to segmental mobility of MMA–DMN copolymer sequences of various content of DMN mers, or reflect relaxation of aromatic side groups.

Nevertheless, these heterogeneities in the copolymer structure must strongly affect the chromatographic behavior, because a part of the copolymer bead (strongly crosslinked "hard" sites) behaves as an adsorption surface and another part capable of substantial swelling ("soft" sites being longer monomer sequences or grafted polymer chains) acts as absorbing centers. However, whether the 3-dimensional copolymer network will behave only as an adsorption surface or whether it will absorb the solute and swell in the chromatographic process depends also on the solubility parameter of the solute and the polymer used.

The presence of "hard" and "soft" units seems to be a general feature of porous bead copolymers used as chromatographic packing that considerably
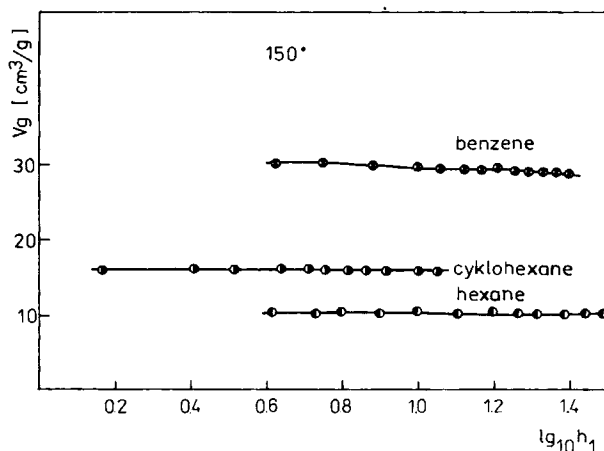
Fig. 7. Specific retention volume of benzene, cyclohexane, and hexane as a function of probe concentration at 150°C.

influences the column separation ability and efficiency.[11] In fact, the hard and soft sites correspond to permeable and nonpermeable parts of the styrene-divinylbenzene copolymers distinguished by Jérabek,[12] if copolymer permeability is a function of the degree of crosslinking and the molecular size of the solute .

It is noteworthy that the transitions observed, expressed by the deviation in the retention diagrams, are at the same position irrespective of the different solvent quality of the probes used, and their different interactions with copolymer are reflected mainly by the differences in the V_g values, which suggests similar retention mechanism or, additionally, that the copolymer bulk is equally permeable for all the probes.

A similar retention behavior is also confirmed by the same character of the dependence between V_g and $\log h$ for benzene, cyclohexane, and hexane, measured at the same temperature (Fig. 7). At the measurement temperature V_g is practically independent of h over a wide range of probe concentration and the supposed retention mechanism here is the equilibrium solution of the probe in the copolymer bulk.[3]

Nevejans and Verzele proved that even rigid, highly crosslinked polystyrene copolymers had rather open, permeable structure due to micropores about 1 nm or more in diameter, formed by the phenylene linkage between two copolymer chains (size of the monomeric divinylbenzene unit).[11]

The same kind of permeability and microporosity must occur for MMA–DMN copolymers as the monomeric DMN unit is even larger than that of DVB and the similar retention behavior for all probes used may to some extent be a proof of a good copolymer permeability for the solutes in the chromatography process.

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