Synthesis and Properties of Porous Copolymers of 4,4′-bismaleimido Diphenyl Methane and Styrene

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SYNOPSIS

Porous copolymers of 4,4′-bismaleimido diphenyl methane and styrene of different molar ratio of monomers were synthesized. The copolymers beads were prepared by the suspension polymerization method in the presence of aqueous solution of poly(vinyl alcohol) and calcium chloride as a dispersing medium. Benzyl alcohol-*n*-decyl alcohol (80 : 20; V/V) mixture was used as the diluent. Independently of the ratio of monomers all copolymer samples indicate stable porosity and high mechanical and thermal stabilities. The results from the SFE show that instead of extraction in a Soxhlet apparatus, some unreacted monomers and diluents remain in the copolymers porous structure. Real compositions of the copolymers found from the results of CHN analyses were different from those assumed. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

High-temperature polymers find extensive applications as matrix for rigid and lightweight fiber reinforced structural composites, metal to metal adhesives, electrical insulations, etc. Because of excellent thermal and oxidative stability, bismaleimides are important representatives of this category. In addition to their thermal stability, bismaleimides possess low moisture absorption properties.[1]

The polymers made from bismaleimides are generally brittle. They are high modulus materials with very low elongation at break. In order to modify their properties, different ways are undertaken. One of them is Michael addition reaction with diamines[2] or copolymerization with styrene.[3]

In this article, porous copolymers formed by suspension copolymerization of 4,4′-bismaleimido diphenyl methane and styrene are presented. Such materials can have interesting properties, but so far have been unknown. Only porous maleic anhydride styrene–divinylbenzene beads of ion-exchanging properties are described.[4,5]

Among porous polymeric materials the most popular are copolymers of styrene and divinylbenzene. Besides them, copolymers with different functional groups gain growing interest.[6–10] Such materials have a wide range of applications such as in waste water treatment, organic synthesis, catalysis, and especially in analytical chemistry as packings for chromatographic columns.

In order to check their usefulness in chromatography, porous structure, swelling, thermal decomposition temperature, and mechanical stability were studied.

To determine substances responsible for copolymers mass loss at low temperatures, supercritical fluid extraction accompanied with gas chromatography–mass spectrometry analysis for some polymer samples were made.

EXPERIMENTAL

Materials and Monomers

Maleic anhydride (Merck), 4,4′-diamino diphenyl methane (BDH), K-54 (Anchor Chem Co.), acetic anhydride (Fluka), and nickel acetate (II) tetrahydrate (POCh Gliwice) were used without further purification in the synthesis of bismaleimide. Styrene, benzyl alcohol, and *n*-decyl alcohol were from Merck while α,α'-azoisobisbutyronitrile was bought from

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Table I Assumed and Real Composition of the BM-ST Copolymers

	Percentage Copolymer Composition (% mol)			
	Assumed		Real	
Copolymer No.	BM	ST	BM	ST
1.	100	0	100	0
2.	95	5	82.7	17.3
3.	87.5	12.5	70	30
4.	75	25	58.8	41.2
5.	62.5	37.5	53.4	46.6
6.	50	50	46.2	53.8
7.	37.5	62.5	30.6	69.4
8.	25	75	23.7	76.3
9.	12.5	87.5	11.7	88.3
10.	5	95	8.6	91.4

Fluka. Solvents used in extraction (acetone, benzene, and methanol) came from POCh Gliwice.

Preparation of Bismaleimide

Bismaleimide was prepared by reacting maleic anhydride with 4,4'-diamino diphenyl methane ($m_p = 91–93°C$) in acetone according to the following two-step procedure:

Preparation of Bismaleimic Acid Intermediate

Maleic anhydride (14.78 g) was dissolved in 80 mL of acetone while stirring in a glass round-bottomed reactor. After cooling it below 20°C, the solution of 15 g of 4,4'-diamino diphenyl methane in 80 mL of acetone was continueously added. The temperature of the reaction was maintained at below 20°C. Maleamic acid obtained in this process was filtered off, washed with acetone, and dried in air at the temperature 60–70°C.

Imidization of the Maleamic Acid

Maleamic acid (18 g), 16 g of acetic anhydride, 0.09 g of nickel acetate, and 3.43 g of K-54 (2,4,6-tri(dimethylaminemethyl)phenol) were stirred and heated up to 65°C and maintained at this temperature for 1 h. The exuding in the reaction water was distilled off. Then the solution was added to 30 mL of methanol. The precipitate was collected, washed with aqueos solution of methanol (50 and 20%), and finally with distilled water. The sample was then purified by recrystallization from methanol and dried at 70–100°C in air.

Preparation of Porous Copolymers of 4,4'-Bismaleimido Diphenyl Methane and Styrene

Porous copolymers of 4,4'-bismaleimido diphenyl methane (BM) and styrene (ST) were obtained by the suspension polymerization method. Copolymerization was carried out in 1 L round-bottomed three-neck glass reactor equipped with a mechanical stirrer, nitrogen inlet, and condenser.

Poly(vinyl alcohol) (21.6 g) and 200 g of calcium chloride were dissolved in 750 mL of distilled water. The suspending medium was then heated to 80°C under nitrogen atmosphere. At this temperature the solution of 44.64 g of 4,4'-bismaleimido diphenyl methane, 12.96 g of styrene, 46.1 mL of benzyl alcohol, 11.5 mL of n-decyl alcohol, and as an initiator 0.17 g of α,α'-azoisobisbutyronitrile was added. The reaction was proceeded for 18 h. Porous beads formed in this process were sucked off, washed with hot water, and extracted in a Soxhlet apparatus with acetone, benzene, and methanol. The purified porous copolymer beads were separated into fractions by the wet sieving. The following fractions were obtained: 0.25–0.20 mm, 20 wt %; 0.20–0.15 mm, 60%; 0.15–0.10 mm, 15%; and smaller than 0.10 mm, 5%. These were first dried at 70°C for 2 h under the reduced pressure, and then for another 2 h at 150°C under atmospheric pressure.

According to this procedure, 10 copolymers of different molar composition of monomers were obtained. Detailed information about their assumed and real composition is gathered in Table I.

Measurements of the Specific Surface Area of Polymers

The specific surface areas were measured on a Sorptomatic 1800 apparatus (Carlo Erba). The deter-

Table II Properties of the Copolymers Studied

Copolymer No.	Specific Surface Area (m^2/g)	q_v	Initial Decomposition Temperature (°C) in Air
1.	45	2.00	380
2.	27	1.94	370
3.	53	1.84	360
4.	70	1.62	360
5.	73	1.50	370
6.	70	1.41	360
7.	123	1.06	340
8.	96	1.41	330
9.	63	1.51	310
10.	71	1.60	300

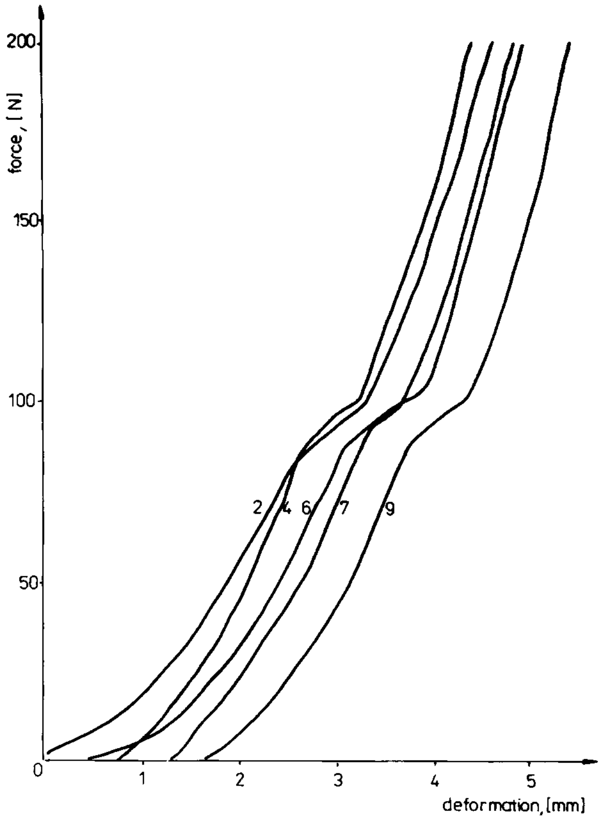

Figure 1 Relationship between deformation of the BM–ST beads in the measuring cell and the acting force. The numbers correspond to copolymer No. in Table I.

mination was based on the measurements of adsorption and desorption of nitrogen on the surface of the studied sample while cooling it to liquid nitrogen. The specific surface areas were calculated by the BET method, assuming that the area of a single nitrogen molecule is 16.2 Å^2.

Volume Swelling Ratio Measurements

The volume swelling ratio, q_v, was determined by placing the copolymer beads from methanol in a graduated cylinder and reading the volume. An excess of benzyl alcohol as the swelling agent was then added, and the volume was read at the swelling equilibrium. q_v was calculated as q_v = final volume/initial volume.[5]

Thermogravimetric (TG) Measurements

The measurements were carried out on a derivatograph (MOM, Hungary) at a heating rate of 5°C/min in the range from 20 to 1000°C in the air. The initial decomposition temperature was determined from the course of the TG curve.

Elemental Analysis

Elemental analyses were made using Hewlett–Packard Model 185 CHN analyser (Palo Alto, CA).

Mechanical Strength Measurements

These studies were made on a universal testing machine INSTRON Model 6212 (Great Britain). Samples of polymer (0.20–0.15 mm) were compressed in the measuring cell (30 mm length × 6 mm i.d.) at a rate of 10 mm/min.

Supercritical Fluid Extraction (SFE) Studies

SFE was performed in a home-made apparatus consisting of syringe pump ISCO-Model 260 D (Isco Inc., Nebrasca, USA) and chromatographic oven Model 504 (Elwro, Wrocław, Poland). Extraction lasted 65 min. The pressure of supercritical CO_2 was 500 atm at 50°C. A flow-rate of liquid CO_2 was c.a. 1.3 mL/min. As an extraction cell, HPLC chromatographic column 5 cm × 4.6 mm i.d. (Merck, Darmstadt, Germany) was used. In each case, the weight of copolymer was 200 mg. The residual solvent and unpolymerized monomers were controlled by Varian 3400–Finnigan MAT ITS 40 gas chromatography–mass spectrometry equipment.

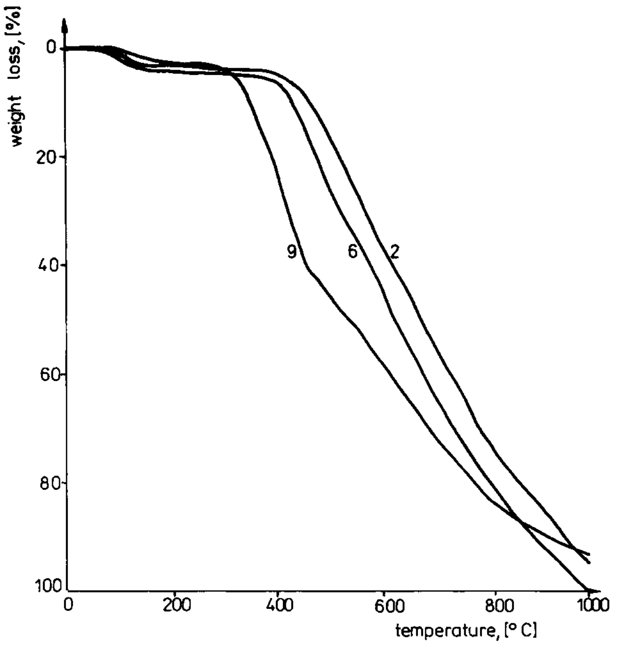

Figure 2 TG curves for the BM–ST copolymers. The numbers correspond to copolymer No. in Table I.

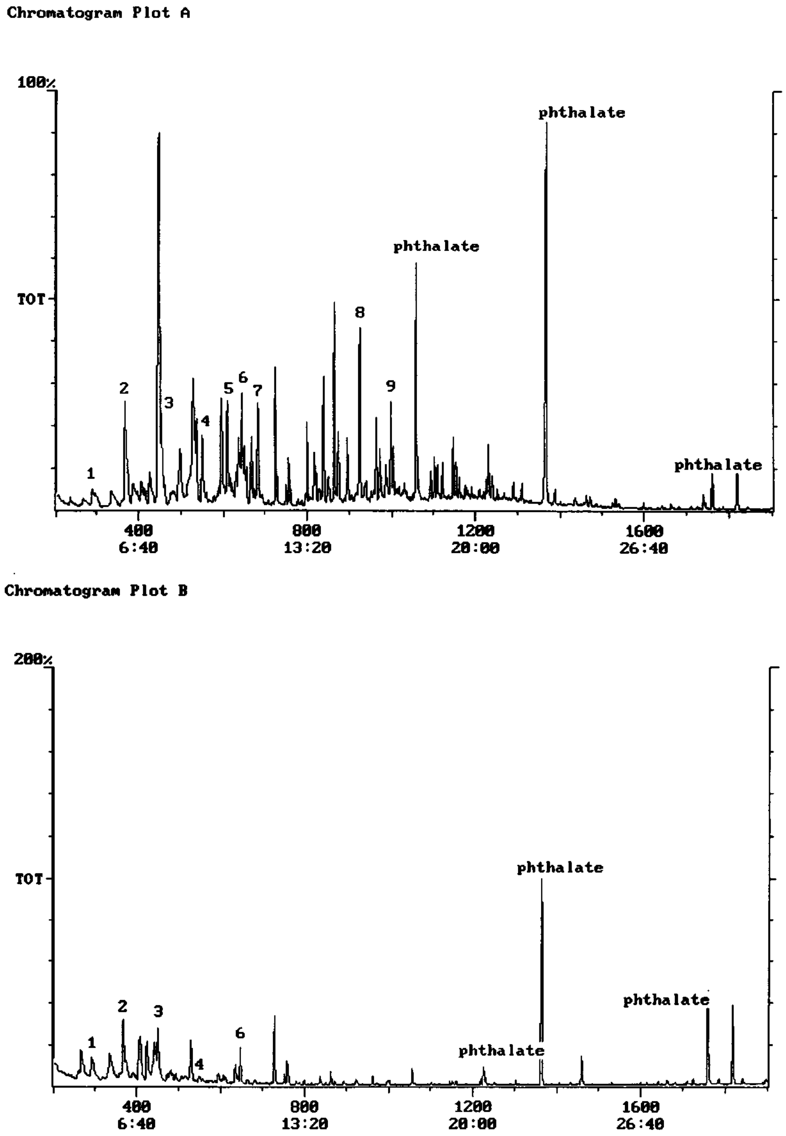

Figure 3 Chromatograms of the substances extracted by SFE from the BM–ST porous polymer samples. Copolymer No. 2 (A), copolymer No. 6 (B). Substances: 1 = styrene; 2 = benzaldehyde; 3 = benzyl alcohol; 4 = benzene ethanol; 5 = phenyl ethyl acetate; 6 = methylbenzene ethanol; 7 = methyl oxime benzaldehyde; 8 = 2-(1-oxopropyl)benzoic acid methyl ester; 9 = decyl alcohol.

RESULTS AND DISCUSSION

The main parameters influencing the internal structure of porous polymers are: the crosslinking agent concentration in the monomer mixture, the volume of the diluents mixture, type, and concentration of diluents in their mixture.

Studies on the influence of monomer ratio on the copolymers structure are possible only under the condition of constancy of other factors effecting the structure. For preparation of the BM–ST porous copolymers there was chosen the mixture containing benzyl alcohol (solvent) and *n*-decyl alcohol (nonsolvent), whose volume ratio was 80 : 20 (V/V) in each experiment. The ratio of diluents to monomers was also constant: 1 : 1 (mL/g).

From the data in Table I presenting the assumed and real compositions of 10 copolymers of the BM–ST, one can see that in the case of the copolymer formed from equivalent mol fractions of monomers and for those samples that contain smaller amounts of the BM, the real compositions are similar to those assumed. For other samples, these values are quite different.

The results presented in Table II indicate that the composition of the copolymers have little influence on the specific surface areas. The highest value is observed for the copolymer containing 30% of the BM. It is important that independently of the copolymer composition the porous structure is stable in a dry state. In the wet state their pore volume increases. The values of the volume swelling ratio q_v confirm this phenomenon. From these results one can see that the copolymer containing 30% of the BM swells the least. For the copolymers of extremely different molar compositions (Nos. 1, 2, 3, 9, and 10) q_v increases significantly. The largest values of q_v indicate the copolymer containing the greatest amount of the BM (No. 1) This fact is astonishing because polymer No. 1 is characterized by the highest crosslinking density. On the other hand, benzyl alcohol is a good solvent for the BM, and probably the polymer composed only from the BM swells the largest.

For five samples of porous copolymers (Nos. 2, 4, 6, 7, and 9) mechanical studies were made. The results presented in Figure 1 show that all samples independently of their composition behave in the same way. Inflexion, in the range of 100 N/cm^2, on the course of the force vs. deformation, is probably caused by a more regular arrangement of copolymer beads in a measuring cell. Above this pressure polymeric materials form a monolith and are resistant to the increase of acting force.

All the studied copolymers are characterized by high thermal stability.[11] The highest decomposition temperatures indicate those copolymers that contain the greatest amount of the BM. Unfortunately, on TG curves, at low temperatures (50–100°C) the mass loss is detected (Fig. 2). In order to determine substances responsible for this phenomenon, SFE and GC–MS analyses were carried out. Chromatograms presented in Figure 3 show that instead of extraction in a Soxhlet apparatus some unreacted monomers and diluents remain in the copolymers porous structure. GC–MS studies identified not only these substances but also products of their oxidation. For sample No. 2, different by-products formed during the copolymerization are also detected.

CONCLUSIONS

The new porous polymers formed from different molar ratio of 4,4′-bismaleimido diphenyl methane and styrene are presented. The copolymers in the form of porous beads are synthesized by the suspension polymerization of the monomers in the presence of benzyl alcohol and *n*-decyl alcohol as diluents, and aqueous solution of poly(vinyl alcohol) and calcium chloride as a dispersing medium.

Independently of the ratio of monomers, all copolymers indicate stable porosity and high mechanical and thermal stabilities. Unfortunately, copolymers with extremaly different molar compositions swell in some solvents significantly. The most useful for chromatographic purposes is copolymer containing 30% of the BM, which swells the least.

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