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POLYMER NETWORKS FOR SOLID PHASE EXTRACTION

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ABSTRACT

Macronet polystyrene (PS) and styrene-ethylene/butylene-styrene triblock copolymer (SEBS) were tested in respect to the sorption of traces of toluene, carbon tetrachloride and 1,2 dichloroethane in water. The studied networks were prepared by a previously developed post-polymerization crosslinking method. The uptake experiments showed a significant sorption efficiency for macronet SEBS especially in the case of carbon tetrachloride. Macronet PS exhibited only a low ability in the sorption of toluene.

INTRODUCTION

Solid phase extraction (SPE) by the use of polymeric resins is a relatively new but well established method for the removal of organics from drinking and salt water, wastes and aqueous biological media [1]. Polymeric sorbents for SPE applications are based on crosslinked macromolecular structures which combine hydrophobic and hydrophilic character. Among them, much attention has been devoted to the use of either non-polar or modified styrene-divinylbenzene (S-DVB) copolymer for its potential use as sorbing agent for various organic contaminants [2,3]. The most usual

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*Author to whom correspondence should be addressed method involves the use of a column filled with the sorbent particles and treatment of the aqueous sample with it. A common feature of all polymeric resins used is their porous character and large surface area which is essential for the improvement of the sorption capacity.

In the present contribution, macronet crosslinked polymers i.e. networks formed by copolymerization or post-polymerization procedures that bear bulky molecules as crosslinkers, were tested in respect to the sorption of some non-polar organic solvents from water. The employment of crosslinkers with molecular size greater than that of divinylbenzene (DVB) - a very common crosslinking agent-taken together with the statistical distribution of crosslinks are claimed to be the principal features which distinguish macronets from S-DVB and other typical macromolecular networks [4,5]. Comparatively with the latter, macronets exhibit high swelling capabilities, they swell in poor solvents and even in non-solvents of the initial polymer and allow the permeation of large molecules [6-8].

The polymers tested in this work derived from the crosslinking of polystyrene (PS) and styrene-ethylene/butylene ABA triblock copolymer (SEBS). The preparation of macronet PS employing mainly chloromethylated aromatic compounds as crosslinkers as well as its properties have been extensively studied [4-11]. Recently, block order macronets were formed by the crosslinking of either SEBS or SEBS / PS blends, with their crosslinks located exclusively in the PS end-blocks, retaining the poly(ethylene/butylene) (PEB) mid-block intact [12,13]. These networks are of hydrophobic type and practically unswellable in water in contrast to hydrogels which exhibit significant water sorption [14-16].Regarding their properties, attention has been directed toward the swelling characteristics in selected organic media.

Materials And Methods

Both PS and SEBS networks were prepared according to the synthetic route reported in detail in previous publications [12,13]. The starting materials were PS (M_w = 260 000, M_n = 118 000) and SEBS (M_w = 116 000, M_n = 107 000) supplied by Dow and Aldrich Chemical Co., respectively. 1,4-Dichloromethyl-2,5-dimethyl-benzene (DCMDMB) synthesized according to an established procedure [17] was used as the crosslinking agent. Following this method, networks of an average number of polymer repeating units between the crosslinks (x_c) equal to 150 were formed. Crosslinking was accomplished by a Friedel-Crafts type reaction between polymer styrene units and DCMDMB under $TiCl_4$ catalysis.

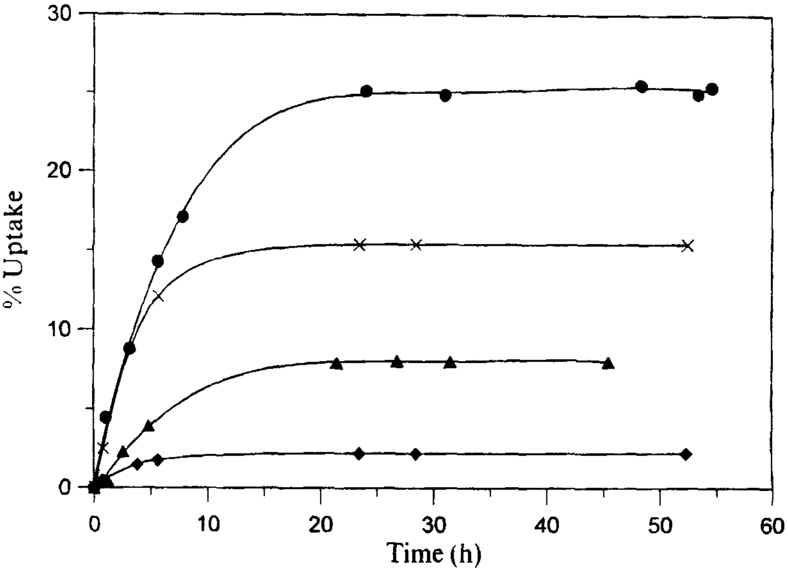

Figure 1. Kinetics of toluene uptake by macronet PS . Initial concentration (●) 413.9 ppm, (×) 363.3 ppm, (▲) 220.4 ppm, (◆) 102.1 ppm.

The sorption capacities of the products were determined for various rather low initial concentrations of toluene, carbon tetrachloride and 1.2 dichloroethane. PS and SEBS were used in the form of particles of approximately 1 mm in dia. 0.1 g of the crosslinked polymer were added to 100 ml of an aqueous mixture of the corresponding organic compound, in a 250 ml flat-bottomed flask under magnetic stirring at ambient temperature. Adsorption was detected by measuring the residual solvent concentration in the mixture at different time intervals, by the use of u.v. spectroscopy method. 5 ml samples were measured in a Hitachi U 2000 double beam u.v./vis spectrophotometer, after filtration with 0.45 μm Millipore filters. Solvent concentrations were determined in the following wavelengths : 285 nm for toluene, 265 nm for CCl_4 and 230 nm for 1,2 DCE.

RESULTS AND DISCUSSION

The sorption kinetics of toluene using PS sorbent is presented in Figure 1. The adsorption capacities were determined for aqueous mixtures with toluene initial

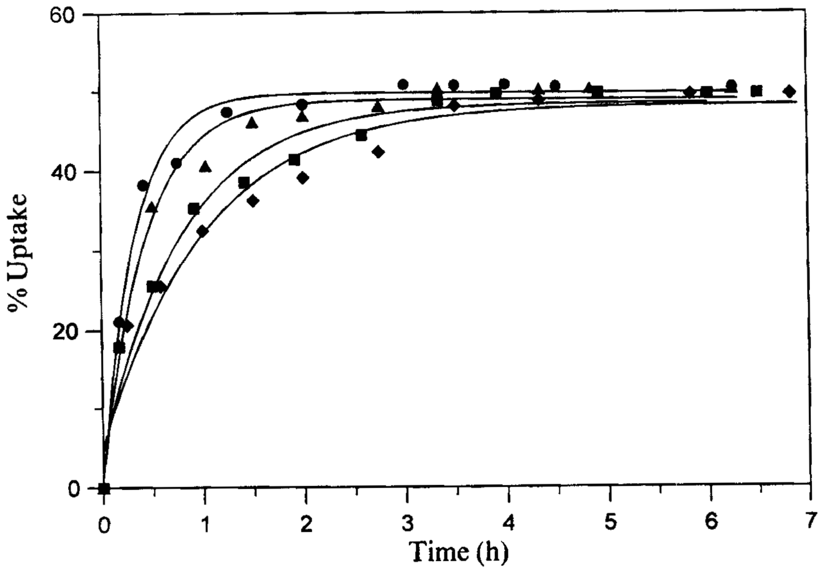

Figure 2. Kinetics of toluene uptake by macronet SEBS. Initial concentration (•) 410.4 ppm, (▲) 319.6 ppm, (■) 210.5 ppm, (◆) 119.9 ppm.

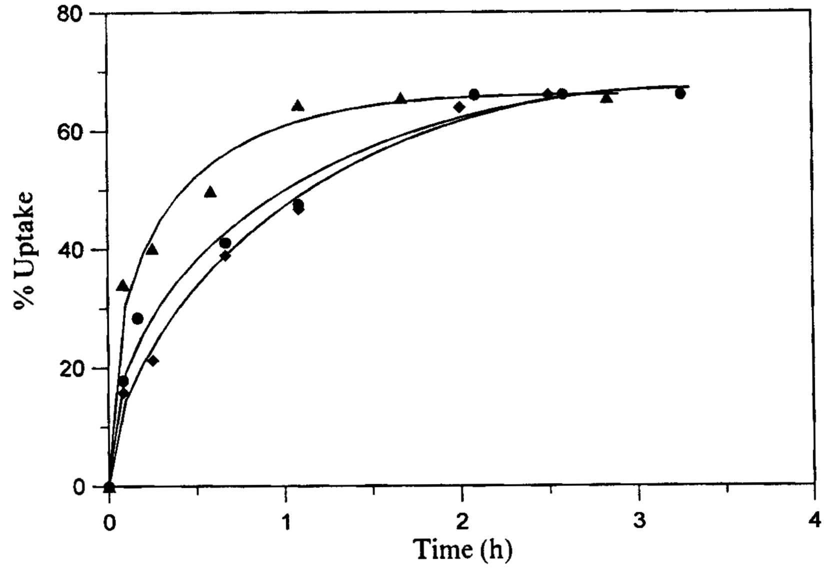

Figure 3. Kinetics of carbon tetrachloride uptake by macronet SEBS. Initial concentration (▲) 355.8 ppm, (•) 242.3 ppm, (◆) 95.36 ppm.

concentration ranging from 102.1 ppm to 413.9 ppm. As it can be clearly seen, the maximum percent uptake for toluene using macronet PS is strongly dependent on the solvent concentration. In fact, as the initial concentration increases from 102.1 to 413.9 ppm, toluene uptake is increased from 2 to 25 %. On the other hand, even though uptakes are considerably different, the sorption kinetics are almost identical and the maximum is attained after approximately 24 hoursfor all mixtures.

The sorption capacity of macronet SEBS versus the same solvent, is illustrated in Figure 2. In contrast to the aforementioned observations for PS, the sorption ability of SEBS does not seem to be interrelated with the toluene initial concentration. Maximum uptake in all cases was determined in the area of 50%, which is much higher than those reached by the use of PS. The better sorbing characteristics of SEBS are also reflected in its rapid adsorption kinetics, since maximum is achieved within a period of 3 to 5 1/2 hours, for the concentration range tested.

The percent uptake for carbon tetrachloride as a function of time, employing SEBS, is plotted in Figure 3. It appears that maximum uptake is attained after 3 hours, approaching to 70% independently on the initial concentration of CCl_4. It has to be mentioned that crosslinked PS was also tested for the CCl_4. extraction but the exhibited uptake was less than 3%.

Figure 4 shows the adsorption curves for 1,2 dichloroethane and macronet SEBS. Uptake is maximum after less than 2 hours of immersion and reaches a 33% level. Similarly to the case of CCl_4, PS exhibited a negligible sorption of 1,2 DCE.

For SEBS, sorption capacity follows the sequence CCl_4 > Toluene > 1,2 DCE which coincides with the solvent per polymer weight uptakes resulted from swelling experiments in pure solvents [13]. This fact could lead us to the assumption that the adsorption capacity is interrelated to the solving ability of the compound sorbed on SEBS. Additionally, the poor sorption capacities attained by macronet PS in good solvents of linear PS like those used, indicates that the better performance of SEBS can be attributed to the presence of rubber poly(ethylene/butylene) segments in this latter polymer.

In conclusion, it can be said that macronet SEBS exhibits good sorption capacity for organic solvents from water with rapid sorption kinetics. The degree of sorption for each solvent appeared qualitatively similar to the swelling of SEBS when immersed in the same pure solvents. Ultimate sorption for CCl_4 seemed to be high enough to suggest this material as a potential agent for water purification. It also should be mentioned that molecular size, polarity and aromatic character of the

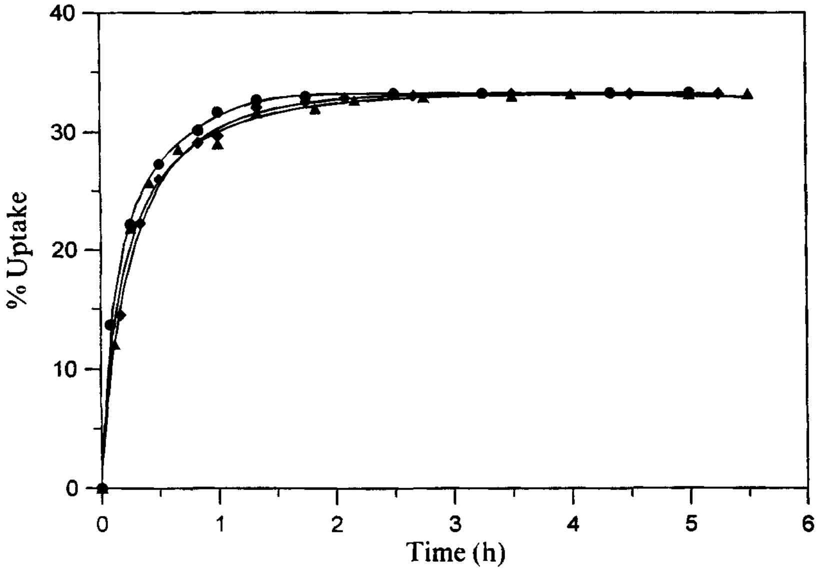

Figure 4. Kinetics of 1,2 dichloroethane uptake by macronet SEBS. Initial concentration (●) 692.2 ppm, (◆) 449.3 ppm, (▲) 202.7 ppm.

solvent, are among the parameters which have to be considered in a further study. On the other hand, macronet PS did not seem to possess any remarkable adsorption characteristics.

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