Macroporous gel-type styrene-divinylbenzene materials

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SUMMARY

     The title materials are produced from macroporous styrene (St)-divinylbenzene (DVB) resins prepared in the presence of a polymer solution as a porogen ; the resulting beads are functionalized upon grafting St-Vinylbenzylchloride (VBC) copolymers through post-copolymerization with residual double bonds. The resulting material has been quaternized by trimethylamine at 35° C. The rate constant of that reaction is then about 6 times higher than that observed for a similar resin (same Cl content and same porous morphology) prepared by direct terpolymerization of St, DVB and VBC.

INTRODUCTION

     Since Merrifield's work on polypeptide synthesis, a high interest is given to the use of functional groups as organic reagents or catalysts supported on crosslinked polymer beads. However, except for the case of acid catalysis, and of course, Merrifield type synthesis, there are not many, if any, industrial development of these supported materials for chemical synthesis. The main drawbacks are the lack of stability which is necessary for long term recycling in heavy industry, and also low conversion or low reaction rates as compared with homogeneous systems, which are the main limitations for their use in fine chemistry. These limitations are due to the slow diffusion of substrates and products in the highly viscous polymer media. The diffusion rates are higher if the material can be swollen by a convenient cosolvent ; but the swelling ability is restricted by the crosslinks and decreases upon increasing the crosslink density. On the one hand, the so-called gel-type resins, initially used in the Merrifield synthesis, have a rather low crosslink density, but the size of the bead is rather large, so that it takes rather long times for the chemicals to diffuse up to the core of the particles. On the other hand in macroporous resins the particle core is easily reached through the pores ; however most of the functional groups are located inside elementary particles which are small but highly crosslinked.
     This paper describes and discusses an approach to combine the main interest of both kinds of beads, i.e. to keep

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a large size particle easy to handle, with high enough porosity and small elementary particles ; but the useful functional groups should be located in regions of low crosslink density. This is achieved by starting from macroporous particles with large pores and grafting inside a functional polymer of a low crosslink density ; the grafting is carried out through a post-copolymerization of the functional monomer with the residual double bonds of the initial macroporous polymer. Similar material has already been used as a support for sulfoxide groups activating an alkylation reaction (1).

EXPERIMENTAL
        - Synthesis of St-DVB resins is carried out by classical suspension radical process in the presence of polymer porogen in toluene as a solvent. Post-polymerization is achieved after swelling in heptane or toluene (15 hours), initiating by benzoyl peroxide, again in suspension process. More details may be found in (1).
        A terpolymer is prepared with polymer porogen in the same conditions as for copolymer (15 % PS in toluene 55 % of organic phase - F_{st} = 0.62, F_{DVB} = 0.195, F_{VBC} = 0.185). The second one is prepared in the presence of octoic acid 31 % - F_{st} = 0.21, F_{DVB} = 0.18, F_{VBC} = 0.61.
        Quaternization is done, after swelling of resin in $CH_3OCH_2OCH_3$ at room temperature for half an hour, by adding a 25 % trimethylamine in water and reacting at 35° C. After reaction, methylal is removed and the resins washed and dried. Kinetics are determined from elemental analysis of %N, weight increase Δp and IR spectroscopy : disappearance of the CH_2Cl band at 1265 cm^{-1} appearance of a $-N^+-(CH_3)_3 Cl^-$ band at 3400 cm^{-1}.
Δp and % N are related by $\% N = \dfrac{14 \, \Delta p}{59 \, (p + \Delta p)}$

% N is related to the VBC molar fraction x by :
        $\% N = 14 \, x/(98.5 \, x + 113)$
the capacity in meq/g being % N / 14.
Characterisation of texture and porosity are described in (1).

RESULTS AND DISCUSSION

        The macroporous initial polymer was prepared upon suspension copolymerization of styrene (75 mole %) and commercial divinylbenzene (DVB) (actually 55 mole % DVB and 45 mole % ethylvinylbenzene) in the presence of a porogen solution of high molecular weight ($\overline{Mn}$ = 170 000 ; $\overline{Mw}/\overline{Mn}$ = 1.04) polystyrene (15 weight %) in toluene (2, 3). The amount of solution (60 weight % of organic phase) was fixed in order to obtain a narrow distribution of large pores shown in figure 1. The porous volume is 1.2 cm^3/g). The infrared spectrum (Figure 2a) of that copolymer shows the 1630 cm^{-1} band assigned to the vinyl stretching vibration, which is the most representative of the residual double bonds of monoreacted units ; the other bands at 1410, 1015 and 990 cm^{-1} have to be corrected from contribution of neighbours.
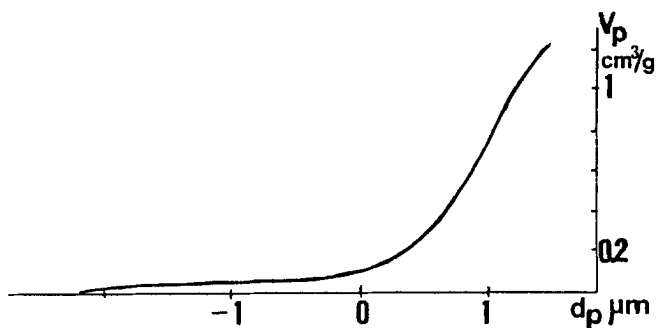
Figure 1. Pore diameter distribution of St-DVB copolymer (log scale) (no difference after post-copolymerization)
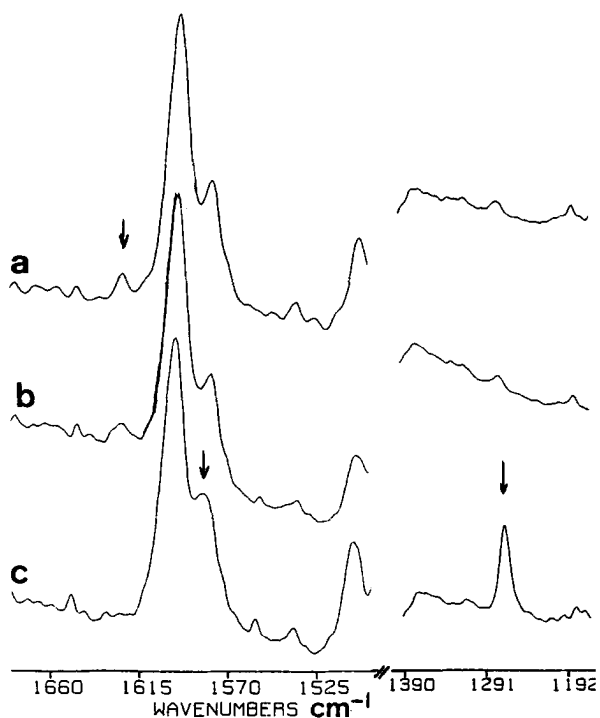

Figure 2. IR spectra of: a) initial St-DVB copolymer, b) after treatment with peroxide without monomer, c) after post-coplymerization with VBC

Quantitative analysis, according to Bartholin et al. (4) indicates that 40 % of the second double bonds of the incorporated DVB units are not participating in crosslinks. In figure 3, the interior of a macroporous bead is shown. The morphology is rather complex and may be described as random agglomerates of particles of a few micron size, partly fused together.
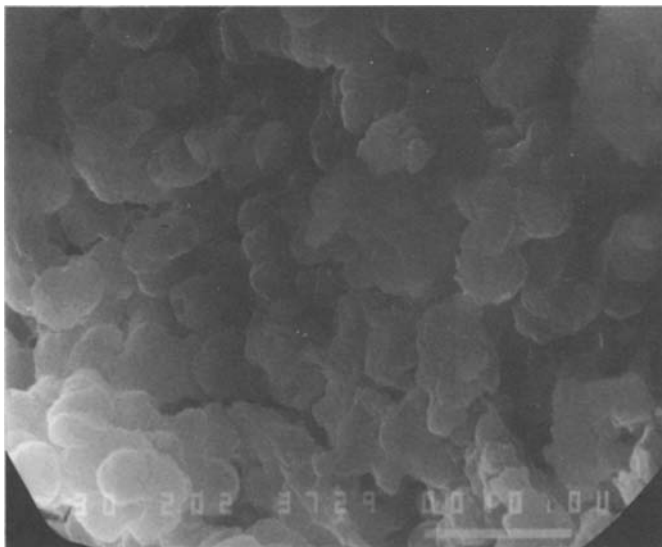
Figure 3. Scanning electron microscopy - Interior of a macroporous St-DVB bead
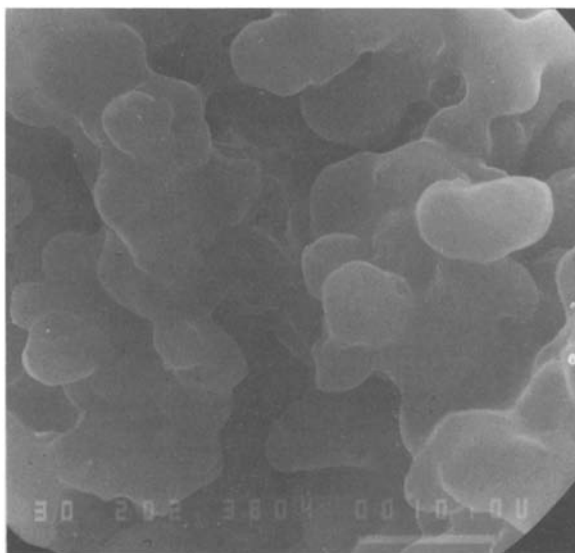
Figure 4. Scanning electron microscopy after post-copolymerization - inside a bead

That macroporous polymer was allowed to swell in
mixtures of styrenic monomer -styrene and vinylbenzylchloride
(VBC) in various compositions- and heptane for about 15 hours,
and then a post-polymerization was carried out in suspension,
initiated by benzoyl peroxide. Due to preferential solvation
of the aromatic monomers, there is a partition of the second
charge between the pores and the inside particles ; then a
large amount of the aromatic monomer is inside these
elementary particles and may be grafted upon copolymerization
with the residual double bonds ; a limited amount of non
grafted copolymer may be extracted (about 16 % of the monomer
engaged) after copolymerization ; that amount is relatively
higher when heptane is replaced by toluene in the swelling
step (about 60 % of the polymer produced). In the infrared
spectrum of the material after grafting, shown in figure 2c,
the bands at 1630 and 1585 cm^{-1} sensitive to the residual
double bonds were strongly reduced, while a new band at
1265 cm^{-1} indicates the presence of chloromethyl groups from
the grafted VBC. As a comparison, Figure 2b shows that
residual double bonds do not react in the presence of peroxide
if no additional monomer is present. Elementary analysis,
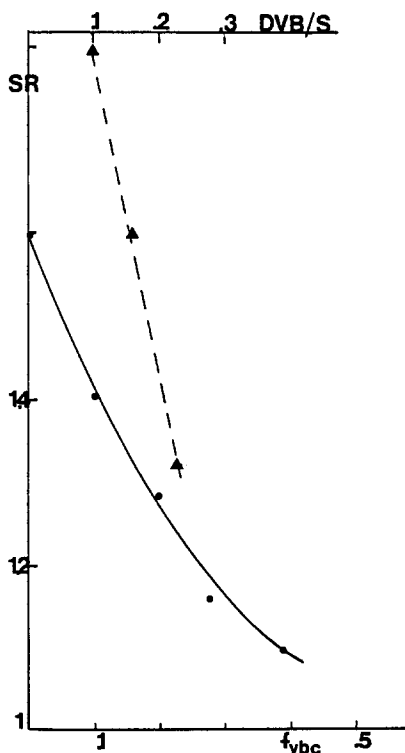weight measurements and calibration of the infrared spectrum

Figure 5. Swelling ratio (SR) in function of VBC molar fraction grafted in
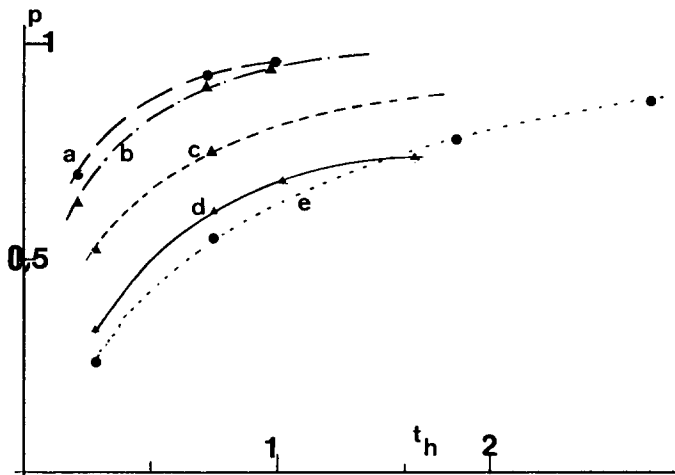the whole product (●) and in function of DVB/St molar ratio in the copolymer▲

Figure 6. a) Conversion (p) in quaternized Me₃N versus time, b) a and e ter-
polymers (15.62 and 4.05 % Cl respectively);b, c, d St-DVB with S-VBC post-
copolymerized (see Table 1)

for the 1265 cm⁻¹ band indicates that about 50 % of the engaged
monomer were grafted. In the case of the comonomer mixture,
there does not seem to be large composition drift. The
interior of the grafted material shows a morphology a little
bit more fused (figure 4) ; however, it is difficult to
conclude from comparison of figures 3 and 4 if the elementary
particles have been enlarged by the grafting process. However,
swelling experiments show that the volume expansibility of the
whole material upon swelling in toluene from the dry state was
strongly reduced by the grafting process (figure 5).

       As a comparison, swelling ratios at different DVB
contents are shown. The swelling ability of a crosslinked
material is limited by its initial crosslink density and the
grafting process has probably used, at least partially, this
swelling ability ; the residual ability to swell is caused by
the retraction of the grafted material during polymerization
(difference between the densities of the monomer and the
polymer).

       The pore size distribution of the grafted material is
very similar to that of the initial material ; it may be
concluded from that, that the polymerization of the grafted
functional copolymer took place inside the elementary
particles more than on their surface. Semi-quantitative
estimate of the consumption of the double bonds of DVB units
allow to conclude that the average crosslink density of the
grafted material is about the same as that of the initial
macroporous polymer, i.e. 1 crosslink for 10 monomer units.

       The grafted material was quaternized to an anion
exchange resin upon treatment with trimethylamine at 35° C.
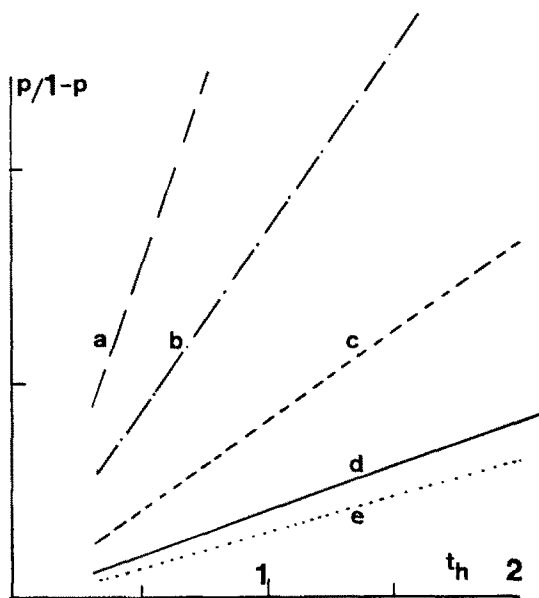Typical kinetic curves are reported in figure 6. It may be

Figure 7. Test of a second order law for materials a to e (see Table 1)

Table 1 - Characteristics of polymers

Product	a terpolymer	b copolymers and	c post copolymerization	d	e terpolymer
F_{VBC} (whole product)	0.61	0.13	0.22	0.16	0.18
F_{VBC} in the graft copolymer	/	1	0.5	0.35	/
% Cl	15.62	4	6.52	4.96	4.05
capacity Cl meq/g	4.4	1.1	1.8	1.4	1.15
porous volume cm^3/g	0.03	1.1	1.1	1.1	0.92
swelling ratio	/	1.38	1.25	1.34	1.61
rate constant k	1.3	3.5	1.1	0.7	0.6
capacity N^+ meq/g	3.14	0.85	1.35	0.9	0.9

shown that the process rate is higher if the chlorine contents of the grafted copolymer is the highest. Figure 6 also compares a material grafted by post-copolymerization (curve b) with a material prepared by terpolymerization of St-DVB and VBC containing the same amount of chlorine (curve e).
The grafted material has a better accessibility. It can be compared with another terpolymer (curve a) of much higher capacity (15.6 % Cl instead of 4.05).
        Treatment of the kinetic data shows that the reactions obey a second order law in all cases (figure 7). The specific

rate constants are reported in Table I. The higher values are observed for the grafted material ; comparison between two polymers with about the same Cl contents (b and e) and the same morphology (both were initially produced using polymer solution as a porogen and have similar porous volume) indicate a factor of six in favor of the grafted material ; in addition, it must be noted that the average crosslink density of the terpolymer is lower. Most probably, the difference points out that the distribution of crosslink inside the elementary particles are not at all the same.

It is well known that the structure of these crosslinked materials, even in the gel type resins is not homogeneous ; due to the higher DVB reactivity, higher crosslinked core of small nodules appear early during polymerization ; most of the residual double bonds are buried inside these nodules (5). These nodules are surrounded by material with lower and lower crosslink density which can be coalesced in a gel. These features are also valid for the elementary particles of macroporous resins, where the coalescence may be more difficult, due to a higher crosslink density and where there are phase separation processes, which cause the large pores to appear.

Upon swelling with functional monomers, the accessibility of the cores to these monomers is high enough for most of the residual double bonds to be consumed, increasing the crosslink density inside these cores, but most of the functional monomers will remain grafted to the surrounding material, and then will finally be located in more accessible and soft regions.

In the case of the terpolymer, the reactivity of VBC is higher than that of styrene and roughly similar to that of DVB ; it results in a high proportion of functional groups buried inside the core of the elementary particles.

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