

Catalysis and polymer networks — the role of morphology and molecular accessibility

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1. Introduction

Organic cross-linked functional polymers (OCPs) have been exploited since long time for many industrial chemical uses and the annual consumption of ion-exchange resins for water treatment alone is in hundreds and thousand tons world wide [1,2]. Their utilization as catalyst carriers in laboratories as well as in a number of industrial processes is also quite important, as they offer potentially much higher capacity for the supported functionality than the conventional inorganic carriers. Acid catalysis is apparently the most important catalytic application of

OCPs, but their use will probably grow significantly in the fields of biocatalysis [3–10] and of supported metal catalysis [11–15].

Functional resins are produced in two basic morphological types.

1. Gel-type (microporous) resins without an appreciable porosity in the dry state, whose interior is accessible only after swelling in the reaction environment.
2. Macroreticular (macroporous) resins with macropores stable even in the dry state, in addition to the micropores generated by the swelling of the polymer skeleton.

Spherical beads with diameter usually in the range 0.3–1.25 mm is the most widely applied form, although some types are also supplied as powder with particles smaller than 0.2 mm. The mechanical strength of the polymer particles could be a problem but this difficulty can be managed through various technical solutions [1].

In view of the undeniable technological success of OCPs, it could be tempting to consider them as

Abbreviations: OCP, organic crosslinked polymers; MTBE, methyl-*t*-butylether; S, styrene; BET, method for measuring surface areas according to Brunauer, Emmet and Teller; DVB, divinylbenzene; ISEC, inverse steric exclusion chromatography; XRMA, X-ray microprobe analysis; PGSE-NMR, pulsed gradient spin echo nuclear magnetic spectroscopy; SSA, *p*-styrylsulfonic acid; MESA, 2-methacryloxy ethylsulfonic acid

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Nomenclature

D	Fick's diffusion coefficient
τ	rotational correlation time

mature, well-understood materials. However, this is not quite true. Exploitation of OCP is still based rather on a trial and error approach than on solid understanding and design of their parameters, especially as far as the nanoscopic features of their morphology are concerned. The aim of this review is both to outline the scientific and technological relevance of OCPs and to offer a contribution to the understanding of their “functioning” at a molecular scale level.

Relatively recently was published a valuable review paper [12] on a subject related to the content of this one. Actually, it is mainly centered on the description of the physico-chemical methods useful to investigate on topochemical features of macromolecular metal complexes $\textcircled{P}-L'-ML_n$ (where \textcircled{P} is the polymer chain, L' the ligating pendant and ML_n the anchored catalytically active metal center). Another valuable review paper by Hodge appeared in 1997 [13]. This is a fine survey of examples of polymer matrix effects on the organic chemistry of polymer-bound reagents. We believe that these papers will offer a quite useful integration to the content of this one and that they all together will provide scientists and technologists with a general view of the potentialities of functional resins as modern chemical tools.

2. Scope of organic cross-linked polymer catalysts in the modern chemical industry

The first experiments with OCP based catalysts were performed during World War II in Germany [16] and USA [17], when it was found that strongly acidic ion exchange resins could be useful in many acid-catalyzed industrial processes. Sulfonated phenol–formaldehyde resins were considered first, but they were quickly replaced by sulfonated S/DVB resins as soon as they became commercially available [1]. From the industrial point of view, they become the most important OCP catalysts continuously operated fixed-bed reactors or suspension reactors (often operated batch wise) are generally applied with these catalysts. Working temperatures range from room temperature up to about 120°C. A few industrial processes catalyzed by OCP-based catalysts are listed in Table 1 and from them by far the most important one is the synthesis of MTBE.

Commercial basic resins for anion exchange in hydroxide form are readily available. They have already been shown to catalyze a number of useful reactions such as the base hydrolysis of esters and nitriles, aldol condensations, Michael additions [18–20]. Basic resins have been also used as catalysts in acylation, esterification, or alkylation reactions [21] and further research of such applications is in progress. In spite of the remarkable versatility of these materials, industrial application of basic polymeric catalysts has been hindered so far by their poor thermal stability (prolonged

Table 1
Selection of industrial acid-catalyzed reactions promoted by OCPs

Product	Reagents	Catalyst
Alifatic esters	Carboxylic acids + olefins	–
Acrylic esters	Acrylic acid + olefins	–
Isopropanol	Propene + water	Macroreticular, 8–10% DVB ^a
Bisphenol A ^b	Phenol + acetone	Gel-type, modified with cysteamine ^c
<i>o</i> -Phenylphenol ^d	Cyclohexanone	Macroreticular
Phenol alkylates	Phenol + olefins	Macroreticular
1-Butene oligomers	Isobutene	Powdered, diameter ca. 30 μm
MTBE ^e	Methanol + isobutene	Macroreticular

^a Divinylbenzene.

^b 2,2-di(4-hydroxy)phenylpropane.

^c The –SH function serves as the co-catalyst.

^d Via dianone, 2-(1-cyclohexenyl)-cyclohexanone.

^e Methyl *t*-butyl ether.

use is possible only at temperatures lower than 60°C) and easy deactivation by carbon dioxide from air.

On the other hand, industrial practice already entered bifunctional catalysts based on OCPs, that is catalysts containing two different types of active centers. Deutsche Texaco developed a commercial process for the synthesis of methyl isobutylketone (MIBK) from acetone [1]. MIBK is obtained from acetone with three consecutive reactions: all of the three reactions can be performed in a single operative step using a sulfonated S/DVB resin, which supports palladium crystallites. Steps 1 (condensation) and 2 (dehydration) are promoted by the acid-base functionality; step 3 (hydrogenation) is catalyzed by the metal crystallites. Another interesting resin catalyst is used for the industrial synthesis of bisphenol A. It contains two different kind of functional groups, acidic sulfonic groups and thioalcoholic groups. This is not strictly a bifunctional catalysts, as the acidic groups are the actual catalytic sites and the thioalcoholic ones act as co-catalyst (or promotor) for the same reaction. However, this material presents some similarity with bifunctional catalysts, in that it shows the possibility of introducing sites of different nature in the same catalyst in order to set up cooperative effects.

Although the idea of utilizing soluble organic polymers as protecting agents of catalytically active metal crystallites has been presented frequently in the literature [22–28], the use of OCPs as designed supports for metal catalysts has seldom attracted catalysis scientists [29]. In contrast with this, the use of polymeric materials as covalent anchors for molecularly defined metal complexes has been much more popular. In spite of the substantial lack of interest from academic scientists, this strategy results to be currently utilized in three significant industrial applications, i.e. synthesis of methylisobutylketone [14,15] and of MTBE (Erdölchemie process) [29] as well as in the dioxygen removal from industrial waters [14]. The persisting evident academic indifference towards the use of OCPs as supports for catalytically active metal crystallites remains surprising. In fact, since the 1980s, Bayer AG has been producing and commercializing a remarkable Pd⁰-based catalyst, active for a very efficient removal of dioxygen (down to the ppb level) from water for industrial use (heating circuits, ultra pure water for microelectronics industry. The active component is metallic palladium, which is deposited

onto the outer shell of the beads (0.5–1.3 mm of diameter) of the functionalized resins. The resins can be either micro- or macroporous and the attached functional groups can be of different nature (quaternary ammonium chloride or hydroxide; tertiary amines), according to the customer's needs. The metal loading is about 1 g d/m³. The catalytic reactor is operated at temperatures up to 70°C, in the presence of the stoichiometric amount of dihydrogen. Under typical conditions, dioxygen concentration in water to be treated is about 8 ppm and it is lowered to less than 10 ppb.

OCPs carrying onium ions, crown ethers and cryptands have been employed since 1975 in organic synthesis for facilitating phase transfer under multiphase conditions (liquid organic, aqueous, swollen polymeric gel). This subject has been thoroughly reviewed in 1988 [30] and research in this area is in progress [31,32]. The technology might become industrially relevant if catalyst recycling and OCPs molecular accessibility will be improved.

Biocatalysis is a very important synthetic technology based on the immobilization of bacteria and enzymes onto organic and inorganic supports [3–5]. OCPs are currently used in this field for the industrial synthesis of aspartic, fumaric, and 6-amino penicillanic acids, in the preparation of lactose-free milk and in the conversion of acrylonitrile into acrylamide (ca. 10,000 t/year) [7–9], and the development of new OCPs-based biocatalysts is pursued also by academic scientists as shown by the recent literature [33–37].

It is our opinion that OCPs will be much more widely and successfully applied when chemical design and tailoring will replace the present “trial and error” approach to the selection of the supports. To this purpose, a deeper understanding of the relationship between the structure and morphology of OCPs and their performances is still required.

In 1969, Haag and Whitehurst from Mobil Oil Co., patented the innovative idea of utilizing macro- and microporous synthetic functional resins as supports for individual metal centers known to be catalytically active under homogeneous phase conditions [38]. The “dogma” of the employment of inorganic supports for heterogeneous metal catalysis was remarkably broken by this proposal which promoted an astonishing scientific activity, reaching its height in the late 1970s and early 1980s. This research field, which is still

considerably alive [39–50], was thoroughly reviewed in 1988 by Garrou and Gates [11].

The dispersion of metal centers inside (generally) commercially available supports is based on the generation discrete species $(\text{P})\text{-L}'\text{-ML}_n$ or $(\text{P})\text{-X-M}^{n+}/n$, where (P) indicates the polymer backbone and L' and X^- represent the functional groups which chemically link, respectively through covalent and ionic bonds, the metal centers to the polymer chains. The first approach was by far the most popular one and the most employed Lewis bases were $(\text{P})\text{-PR}_2$ groups. In the swollen state, the metal-containing “molecular” units were expected to behave respectively as the analogue homogeneous catalysts $\text{L}'\text{-ML}_n$ although the material as a whole was expected to behave as a heterogeneous catalyst (“hybrid phase catalysis”) [51].

Unfortunately, this rush to the perfect catalyst able to produce thousands of papers and patents, occurring especially in 1970s, did not succeed in producing any real industrial breakthrough. In fact, in spite of numerous claims of “reusability” with “no substantial loss of activity” and with “no appreciable loss of metal”, hybrid phase catalysis gradually lost popularity. However, in recent years research in this direction seems to “gain a momentum” again. Very promising olefins epoxidation catalyst, which seems to be really a hybrid one (i.e. without any perceivable metal leaching), has been recently announced [52,53]. The catalyst is a macromolecular polybenzimidazole (macro- and microporous) complex of Mo^{VI} , which catalyzes the epoxidation of cyclohexene, propene and other alkenes with *t*-butylhydroperoxide under technologically interesting conditions [53–55].

One of the major drawbacks of OCPs is represented by their mechanical properties. In order to overcome this problem, some attempts to combine the superior mechanical stability of inorganic materials with advantageous chemical properties of OCPs in composites materials have been made. The composites, consisting of inorganic carrier with an OCP dispersed in its macropores [56,57] could be used in special applications, like catalytic distillation processes [58]. Sharma and co-workers claim that the sulfonated, strongly acidic composites based on an inorganic carrier have a better thermal stability than the conventional OCPs [56]. However, this does not seem to be very likely, as the desulfonation rather

than destruction of the polymer backbone bring out the thermal degradation of strongly acidic OCPs.

3. Synthesis of OCPs

Extensive reviews on this subject are available [21,59,60]. Therefore, we will provide here only a brief outline of the most widely utilized procedures for the preparation of OCPs in beaded form, the most relevant to industrial applications. Moreover, we will focus our attention to S/DVB resins, which are by far the most important catalysts precursors. They are usually obtained by suspension polymerization in water, under strictly controlled conditions. At the beginning of the reaction, the organic phase, dispersed as small droplets in the aqueous one, consists of a homogeneous mixture of styrene, divinylbenzene and a porogenic agent (only if a macroreticular (macroporous) material is desired). In the absence of a porogen gel-type (microporous) resins are obtained. For a stabilization of the macroporous morphology cross-linking degrees exceeding 8–10% is required. Pore sizes, pore size distribution and specific surface areas of the macropores can vary over a wide range, according to the polymerization conditions.

Functionalization of the polymer can be achieved either by utilization of already functionalized monomers (a relatively uncommon approach) or using a suitable polynier-analogic reaction with the already formed polymer. S/DVB resins can be functionalized upon well-established procedures (see, for example, Ref. [60]). Sulfonated materials are nearly exclusively prepared by direct sulfonation of polystyrene with concentrated sulfuric acid. Other functional groups can be introduced upon starting from lithiated or chloromethylated polystyrenes. Treatment of S/DVB resins with *n*-butyllithium in ethylenediamine yields lithiation of about one quarter of the aromatic rings. Metalation occurs mainly at the *meta* position (regioselectivity ca. 65%). Better results (higher degree of lithiation and regioselective functionalization of the *para* position) are achieved if polystyrene is halogenated (with bromine or, better, iodine) prior the reaction with alkyllithium derivatives. Chloromethylation can be effected by the Friedel–Craft reaction of methoxychloromethane with phenyl rings in the presence of tin tetrachloride or iron trichloride as

the catalyst. The regioselectivity is favorable for the substitution in *para* position.

4. Micro- and nanomorphology of OCPs

Whenever the comparison of the activity of OCPs catalysts with their homogeneous analogs is possible, the specific activity of the polymer-supported catalyst is usually lower than that of the homogeneous one. Mass transport is often indicated as the culprit and in some cases it may be true. However, the analysis of available information [11] and direct experimental evidence [61] show that in most cases the observed reaction rates are the results of intrinsic kinetics rather than of diffusional restrictions. The catalytic performance of OCPs catalysts depends critically on both the nano-environment surrounding the active centers and their accessibility. Accessibility of the active centers in these materials is dramatically affected by the extent of swelling of the polymer mass in contact with the reaction medium, both in the gel-type and in the macroreticular OCPs, as it is very schematically depicted in Fig. 1.

In a typical macroreticular strongly acidic ion exchange resin, less than 5% of the all the acidic active centers are located at the macropore walls accessible without swelling. Remaining 95% of active centers become accessible only when after contact with a liquid swelling of the polymer mass opens additional porosity. Hence, for the assessment of the performance of OCP-based catalysts the knowledge of the swollen-state morphology and the influence of the polymer gel environment on reacting molecules is of a great importance. In spite of this, only very few quantitative studies on the relationship between catalytic performance and structural or textural properties of the polymeric supports have been carried out up (see for example [62]). Moreover, we feel that the information available on the nanomorphology of OCPs is still scattered, especially in the case of gel-type OCPs. This section will be devoted to give a short critical overview of the methods which have been used for the characterization of the morphology of synthetic OCPs both at the micro- and nanoscopic (i.e. quasi-molecular) level [63].

One of the most striking differences between inorganic solids and OCPs is the swelling ability of these

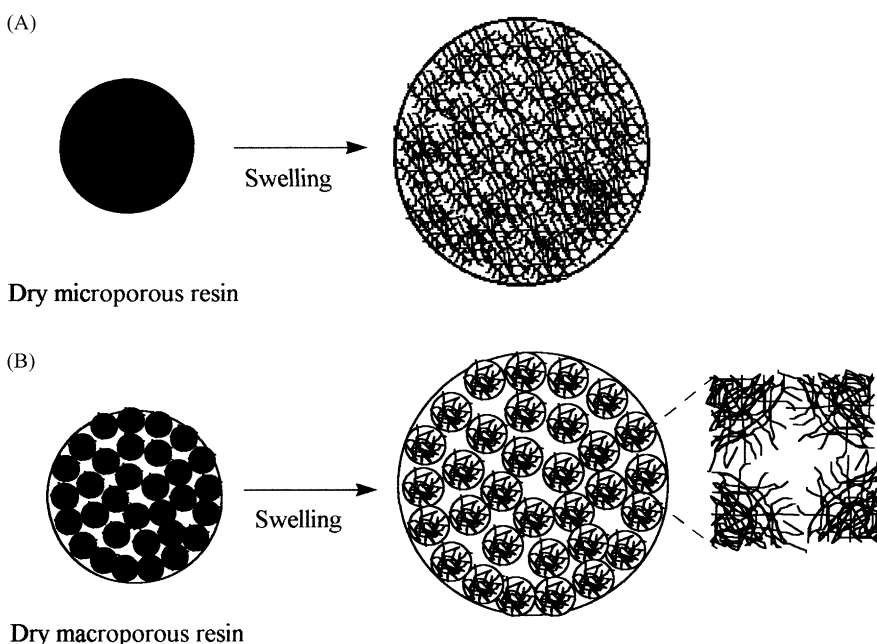


Fig. 1. Schematic representation of changes in the morphology of microporous, gel polymer head (A) and macroporous polymer bead (B) during swelling. The scheme depicts the basic principles only — it is not drawn to scale.

organic materials. When a liquid able to solvate the polymer chains is put in contact with the resin, solvent molecules penetrate into the polymer network and the swollen gel is formed. The gel can be considered as a quasi-solution in which osmotic pressure arises. As a consequence, the polymeric chains stretch out and elastic forces opposing to swelling build up. The process stops when the balance between osmotic and elastic forces is attained.

Swelling effectively separates the polymeric chains and therefore, enhances dramatically the accessibility of the inner part of the polymer network. It is worth to mention that the total length of the chains in a typical S/DVB resin is as high as about 1.4×10^{-9} km/g (about ten times the Earth–Sun distance), corresponding to a surface area of about 2000–4000 m²/g. Swelling can make a substantial fraction of this extremely high surface available for interactions with molecular species diffusing through the gel. It is evident that the polymer materials offer potentially much higher supporting capacity than conventional rigid inorganic carriers. This extensive supporting capacity resides in microporous cavities with nanometer dimensions in the swollen polymer matrix of either gel-type or macroporous resins. In addition to these “temporary” (swelling-dependent) micropores, the macroporous materials possess also macropores more or less independent of swelling (Fig. 1). As pointed out above, this permanent porosity is created during the polymerization in the presence of a porogenic miscible with the monomer mixture. The beads of the macroporous resins are aggregates of nodules formed as the consequence of the phase-separation of the growing polymer network from the porogenic solvents in the course of the polymerization process and the spaces between these nodules form the macroporous part of the resin porosity. Overall morphology of the resulting material depends both on the degree of crosslinking of the polymer and on the amount and type of the porogenic solvent (see Section 3) [64]. It must be again emphasized that in the overwhelming majority of applications of the macroporous resins, the vast majority of the interactions with molecules from surrounding fluids occurs inside of swollen polymer mass and not on the macropore walls. Therefore, data on morphology or surface area of these materials determined by conventional methods on unswollen, dry materials are

for correlation with the application properties only seldom useful.

As a rule of thumb, the higher is the cross-linking degree (nominal content of the cross-linking co-monomer), the slower is the diffusion of the molecules of reactants inside the polymer mass. However, at least in the case of the most common type of OCPs, co-polymers of styrene and DVB, crosslinks are not homogeneously distributed in the polymer mass. Due to higher polymerization reactivity of DVB than styrene, the polymer formed in the initial stages of the polymerization, is more rich in DVB than the polymer formed later and hence, the local crosslinking can be very inhomogeneous and simple information on the nominal degree of crosslinking may be insufficient. It concerns especially the macroporous resins, which usually have rather high degree of crosslinking, necessary for to keep the macropores from collapsing. In these materials may be the inhomogeneous distribution of the crosslinking particularly apparent, as the cores of the nodules, which are formed in the initial stages of the polymerization, are more rich in DVB than the outer shell forming the macropore walls. The diffusional constraints can be outweighed if the nodules are very small. This can be easily understood if the concept of the Thiele modulus is applied to the nodules of polymer mass [1]. Whatever point of view is adopted, the accessibility of the supported functionality in macroporous OCPs depends on the polymer morphology, both at the micro- and nanoscopic level. In these materials the primary role of the macropores is not to provide the active surface, but mainly to facilitate the contact between the molecules of the reactants and the gel part of the COPC, where most of the active centers reside [65]. Overwhelming majority of the active sites is located in the cavities of the swollen polymer matrix, which can be considered as “microreactors” with molecular-scale dimensions. It appears that the effective design and optimization of these “microreactors”, i.e. of suitable polymeric materials for specific applications, do require the detailed characterization of the chemical structure and of the physico-chemical features of the microenvironment inside the gel “cavities” [63].

The characterization of dry solid materials is usually carried out by means of well-established methods, including nitrogen adsorption (BET), nitrogen capillary condensation or mercury intrusion porosimetry

[66]. However, it has been already pointed out that information on the texture of OCPs in the dry state is only seldom relevant to their properties in the working state, i.e. the swollen state. The quality of the information can be largely improved if swollen materials can be dried with only minimum (or even better without) collapse of the structure of the expanded polymer network. This task can be accomplished by means of either very careful treatment with suitable solvents [67] or through lipophylation [68].

The textural features of swollen OCPs has been investigated by means of several physico-chemical techniques. The attention has been focused on the influence of the macromolecular network on the behavior of either the swelling agent or molecular probes dispersed in the polymeric gel. For instance, pore sizes in the swollen gel can be evaluated from the depression of the freezing point of the swelling agent (thermoporometry) [69]. Information on porosity can also be gathered from the analysis of the process of controlled evaporation of the swelling agent. However, these techniques provide only a “fingerprint” of the materials rather than an insight into their texture. Among the currently available methods, inverse steric exclusion chromatography (ISEC) yields the best quantitative assessment of the nanomorphology of swollen OCPs. This method was proposed independently for this purpose by Halász [70] and Freeman [71]. The swollen material to be characterized is employed as the stationary phase in a liquid chromatography column. Measured are then elution volumes of solutes of known molecular size at conditions when the partition of a solute between the bulk liquid and the examined solid is governed by steric (entropic) factors only. A proper mathematical treatment of the ISEC data may provide information

on pore volume distribution of pores of sizes from hundredths of manometers down to molecular dimensions [72,73]. The description of the morphological features is based on the following assumptions: (a) the pore system can be described using simple geometric models; (b) it can be modeled as a discrete set of fractions, each consisting of simple pores of a single size only.

Macropores of the macroreticular resins can be acceptably described in terms of the conventional cylindrical pore model (pore diameter and volume). Characterization of the morphology of swollen polymer mass using the model of cylindrical pores can be successful from the mathematical point of view but the values of parameters (e.g. pore volume) may be unrealistic [72]. A geometrical model developed by Ogston [74], in which pores are defined by spaces between randomly oriented rigid rods, is for the three-dimensional polymer network a better approximation. According to this model, the pore size is described as the total rod length per unit of volume (polymer chain concentration, n/m^2). The final output of the ISEC of the swollen-state resin morphology is the information on both the distribution pattern of the macropores (if present) and the volume distribution of the differently dense gel fractions in the swollen polymer mass. The quantitative description of the micro- and nanomorphology of swollen polymeric supports provided by ISEC helps in explaining how the morphology itself was affected by the polymerization conditions and how the morphology affects the microenvironment inside the swollen polymer mass [62,75,76].

During the last two decades the problem of characterization of swollen polymers was addressed also by means of several approaches, based on the physico-chemical methods listed in Table 2. The molecular

Table 2
Physico-chemical methods applied to swollen polymer characterization

Method	Information	Reference
Diffraction ^a	Nanoscopic morphology	[48]
EPR of paramagnetic probes	Accessibility ^b , mobility ^b	[49–52]
NMR of confined solvent	Accessibility ^b mobility ^b	[54,55]
ISEC	Size and volume of “pores”, surface area	[39–41]
X-ray microprobe analysis	Distribution of functional groups	[45,57]
EPR of paramagnetic probes + ISEC	Swollen state morphology, accessibility ^b , mobility ^b	[43]

^a Light, neutrons and X-ray.

^b Swelling solvent or dispersed probes.

accessibility of OCPs can be roughly estimated by means of X-ray microprobe analysis (XRMA). For instance, millimeter-sized particles of polystyrene were chloromethylated, then functionalized with phosphino groups and eventually the phosphinated material was reacted with rhodium(I) complexes. The penetration of the reactants towards the core of the particles was estimated from the distribution of chlorine, phosphorus and rhodium atoms in the material as determined by XRMA after each step. The higher the cross-linking degree, the more difficult is the penetration of the reacting species [77,78]. In a similar way, sulfonic groups were gradually introduced, under controlled conditions, in S/DVB resins [79]. The most accessible domains are sulfonated first, followed by the denser polymer mass fractions. Subsequent catalytic tests has made possible to assess the activity of the acidic centers in different parts of the polymer mass and to correlate it with their relative accessibility.

Diffraction studies disclosed the heterogeneous nature of co-poly(*N,N*-dimethylacrylamide/methylenebisacrylamide)s gels [80]. The largest part of the gels is occupied by a solution-like phase, in which the polymeric component has a homogeneous chemical structure. The remainder is occupied by a second highly heterogeneous phase, formed by pockets of almost pure solvent and a polymeric precipitate whose composition ranges from practically pure poly(*N,N*-dimethylacrylamide) to practically pure poly(methylenebisacrylamide).

ESR spectroscopy of suitable paramagnetic probes dispersed into polymeric gels has been widely exploited to estimate molecular mobility in swollen OCPs (e.g. [81–84] or see recent review [85]). Both organic (stable nitroxide radicals) and inorganic (transition metal ions with unpaired electrons) probes have been considered. The method, as applied to microporous materials, was pioneered by Regen [81] in 1975, Watanabe et al. [84] used the concept of critical volume in connection with the effects of the confinement of hydrated Cu^{2+} ions inside of polymeric gels. The critical volume is the minimal volume of solution required for free molecular motion of solutes [86]. For a single hydrated Cu^{2+} ion, the critical volume is found to be $8 \pm 1.2 \text{ nm}^3$. The confinement of a solution within a polymeric gel limits the solution volume available for the motion of solute molecules. Thus, when the size of the cavities drops below a certain

critical value molecular mobility of the molecules in solution is severely hindered. This has been confirmed also by EPR investigations on aqueous solutions of Cu^{2+} dispersed inside poly(*N,N*-dimethylacrylamide) gels featured by cavities diameters ranging from 0.6 to 6 nm [82]. Rotational mobility is apparently lost only in the narrowest (0.6 nm) cavities.

NMR spectroscopy of the swelling medium can also give valuable results. From measurements of spin-lattice relaxation time, T_1 , of ^{13}C nuclei, the viscosity of toluene was shown to be about 50 times higher inside the cavities of a polymeric material than in bulk solution [87]. The investigated polymer was a gel-type S/DVB resins functionalized with alkylphosphonium cations, which had been employed as a phase transfer catalyst [88].

The combination of the results obtained from different independent techniques is expected to yield a deeper understanding and reliable physical modelling of the investigated systems. As to the chemistry of functionalized resins, ISEC characterization of swollen polymeric materials has provided a very sound basis for the interpretation of the differences between the catalytic behavior of acidic ion-exchange resins and analogous molecular acids. As a result, a quantitative description of the effects of the heterogenization of the acid catalyst on its activity has been achieved [62]. ISEC has also been employed in combination with a number of other techniques. Jeřábek, et al. [76] studied a set of highly cross-linked macroporous S/DVB resins by means of ISEC and fluorescence spectroscopy. The BET surface areas were also measured in the dry state. The employed fluorescent probe was covalently bound to the polymer chains during the polymerization. The investigated resins were swollen in a number of different solvents and the values of τ_{max} in the fluorescence emission spectra were recorded. It is known that the value of τ_{max} depends on the solvent–solute interaction (solvatochromic effect) and the extent of the solvatochromic effect in the swollen polymers was used to assess the accessibility of the polymer network to the molecules of the swelling agent. This investigation showed that accessibility depends dramatically on the nature of the porogenic agent employed during the synthesis of the resins. When acetonitrile was used as the porogen, τ_{max} in the swollen polymer mass was practically independent of the employed swelling medium, either a good or

bad one. It was also very close to the value observed for the dry solid. The absence of any solvatochromic effect demonstrated that no interaction between the polymer-attached fluorescent groups and the swelling solvent had occurred, i.e. the polymer network was in fact poorly accessible. On the contrary, when the polymers were synthesized in the presence of toluene as the progen, the solvatochromic shifts were not very different from those observed in solution. Accordingly, the solvent-probe interaction was quite similar both in the solutions and in the gels, i.e. the polymer-bound fluorescent moieties were almost as accessible as in true solution state. These findings were fully confirmed by ISEC. Substantial fractions of the polymer mass of the materials synthesized in the presence of acetonitrile did not participate in the chromatographic process during ISEC runs, i.e. they completely excluded any chemical species. On the contrary, the whole polymeric mass appeared to take part to the chromatographic process during ISEC runs in the case of materials prepared in the presence of toluene. These different behaviors are the consequence of the textures produced by the different porogens. Acetonitrile is a bad solvating agent for the growing polymer chains, hence it favors phase separation during the polymerization. As a consequence, the obtained polymers are formed by very dense clustered particles, separated by void volumes, which are practically permanent pores. The polymer mass maintains a collapsed, compact structure also when it is in contact with potentially good swelling agents and is poorly accessible. Toluene is a good solvating agent for the polymer chains growing during the polymerization. Under these conditions not only dense polymer mass is formed, but also appreciable expanded fractions, effectively less cross-linked. These results call the attention to the inadequacy of the dry surface area techniques (e.g. nitrogen adsorption/desorption measurements) for the assessment of the accessible points on a polymer surface in the swollen state. They also point out that in the case of macroporous resins both the macropore system and (even more important) the morphology of the polymer mass must be taken into account.

Recently we have studied a number of swollen gels of poly(*N,N*-dimethylacrylamide) cross-linked with methylenebisacrylamide (1–8 mol%) [75,89]. The dry resins are swollen with solutions of TEMPONE (2,2,6,6-tetramethyl-4-oxo-1-oxyl-piperidine, a stable

radical) in water, methanol, dichloromethane and tetrahydrofuran. After swelling, the EPR spectra of confined TEMPONE are recorded for each sample. In most cases, the spectra have shown that the molecules of TEMPONE are still in the fast rotation regime, although their rotational mobility is generally lower than in solution. Under these conditions straightforward analysis of the spectra provides the values of the rotational correlation time (the time required for a molecule to sweep the angle of one radian). Only in tetrahydrofuran is the rotation so slow to prevent a direct calculation of τ from the spectra. The swollen gels have been characterized also by means of ISEC, using the same solvents as mobile phases during the chromatographic runs.

The distribution patterns of polymer chain concentration and the values of τ of TEMPONE inside of the swollen networks are quantitatively correlated as illustrated in Fig. 2. On the basis of chemical intuition, the rotational speed of TEMPONE is expected to decrease, as the polymer chain concentration of the network gets higher. On the basis of the relationship between the viscosity of concentrated fibers solutions and their concentration given by Nicodemo and Nicolais [90], the Stokes–Einstein law and the Ogston's model, the apparent correlation reported in [75] is fully rationalized. The observed and the predicted τ values are in very close agreement and, remarkably, the best fit is obtained when the value of the molecular radius of TEMPONE (the only adjustable parameters of our model) equals 0.32 nm. Similar finding had been previously reported by Freed and co-workers [91]. In conclusion, the polymeric aqueous gels obtained from lightly and medium cross-linked dimethylacrylamide resins, described in [75], can be depicted as concentrated, viscous solutions of polymer chains, in which a quasi-homogeneous chemist can be envisaged.

The successful application of these two independent techniques prompted us to apply also a third one, namely Field Gradient Spin Echo NMR Spectroscopy (FGSE-NMR) [92,93], for the assessment of the translational mobility of the molecules of the swelling agent. The translational mobility is expressed by the Fick's diffusion coefficient, which depends on the newtonian viscosity of the liquid, hence on the polymer chain concentration in the case of a swollen polymer network. In particular, D is expected to decrease as the polymer chain concentration increases (Fig. 3).

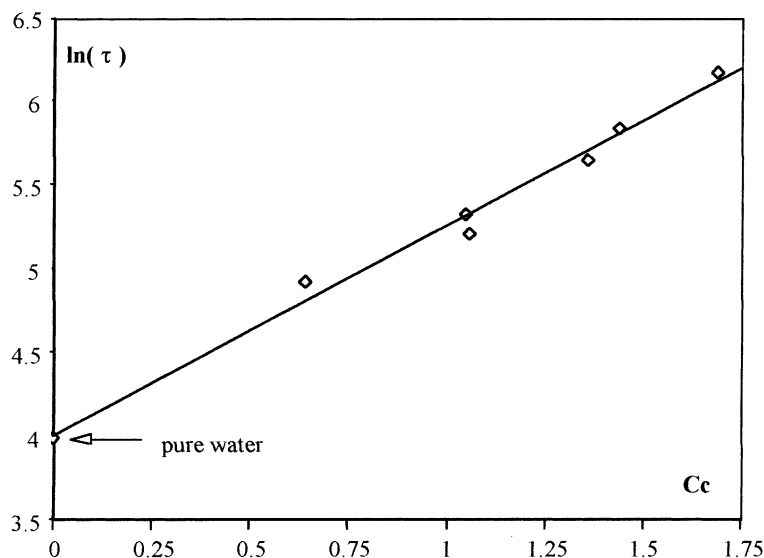


Fig. 2. Experimental relationship between rotational correlation time of TEMPONE, τ dissolved in water confined inside water swollen variously cross-linked poly(dimethylacrylamide) resins and their weighed average polymer chain density C_c (room temperature), (from [75], courtesy of American Chemical Society).

This approach has been applied to investigate four gel-type resins, with chemical structure closely related to the polyacrylamides mentioned above and nominal cross-linking degrees ranging from 2.0 to 8.1% (mol/mol) swollen in water dichloromethane and tetrahydrofuran. Not only the linear correlation between $\ln \tau$ and the polymer chain concentration (c) holds for all of the materials and all of the solvents employed, but it is also observed between $\ln D$ and c . In other words, a linear relationship is eventually demonstrated between the self-diffusion coefficient of the swelling agent and the rotational correlation time of the paramagnetic probe employed in the ESR experiments inside of the swollen microporous resins [94].

We have also investigated model hydrogenation palladium catalysts based on ion-exchange resins [95–101]. The polymeric supports have been synthesized by co-polymerization of sulfonated monomers such as SSA or MESA with several co-monomers, in order to obtain hydrophilic, lipophilic, and amphiphilic [102] materials. These supports, in acidic form, easily react with palladium, copper and nickel acetates in acetone/water (1/1) and exchange hydrogen ions with the relevant metal centers.

Upon treatment with dihydrogen or NaBH_4 in ethanol, the palladium-exchanged resins yield resins-supported palladium catalysts [95]. One set of palladium catalysts, based on amphiphilic resins obtained from styrene, MESA and MBAA as the cross-linker (cross-linking degree 1–6%, mol/mol), has been thoroughly characterized by means of ISEC, ESR and PGSE-NMR and thereafter tested in the model hydrogenation of cyclohexene [100,101]. Under such conditions (kinetic regime) that mass transport phenomena do not affect the catalytic process, the reaction rate is independent of the physico-chemical features and accessibility of the supports, as assessed by means of the above mentioned techniques [101]. However, when mass transport phenomena are rate determining (diffusional regime) the highest apparent rate is observed for the most accessible materials [101].

Although, these results should be regarded as still preliminary ones, they indicate that the combined exploitation of ISEC, ESR and PGSE-NMR may significantly improve our understanding of the character of the reaction environment inside swollen polymer gels and serve for evaluation of the nanomorphology and molecular accessibility of functional resins to be employed in catalytic application (Fig. 3).

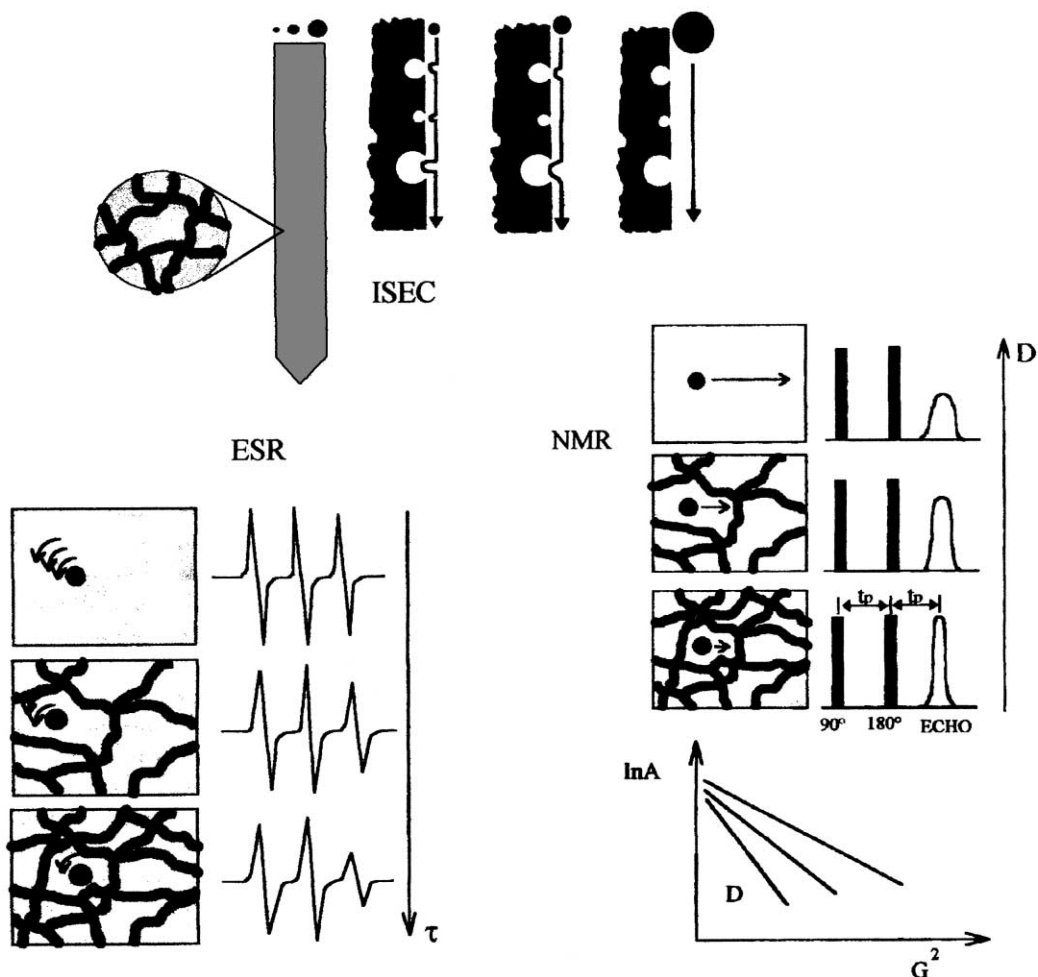


Fig. 3. Schematic illustration of the expected relationship between outputs of ISEC, ESR and PGSE NMR techniques. (a) ISEC yields a quantitative estimation of the polymer chain concentration of a swollen polymer network. The larger its value, the smaller; (b) The rotational mobility of a paramagnetic probe (assessed from the broadening of its ESR lines) and (c) the translational mobility of the molecules of the swelling liquid (assessed from the change of intensity of their spin-echo).

5. OCPs catalysts in action: strongly acidic ion exchanger catalysts

In this section we illustrate the specific problems and effects associated with resin catalysts on a few examples of studies and applications of the most widely used and investigated polymer-based catalysts that is strongly acidic ion exchangers. Thanks to their well-defined chemical nature they may be regarded as a model most suitable for demonstration of the special properties of the OCPs.

Depending on the reaction conditions, the character of the environment of the swollen polymer gel in which the reactions on OCPs proceed may change between state similar to that of liquid solution typical for homogeneous catalysis and a state more close to the solid–liquid interface typical for conventional heterogeneous catalysts. It of course has a strong impact on the way how the polymeric backbone influences the course of the supported reaction.

In the aqueous environment the active agent in the ion exchanger catalyst is the hydroxonium cation,

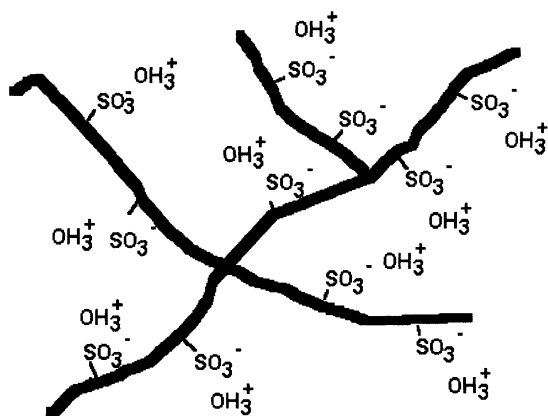


Fig. 4. Hydrated protons as acidic centers in water-swollen ion exchanger catalysts.

more or less freely mobile in the vicinity of the anionic groups bonded to the polymer chains [103,104]. This situation is schematically depicted in Fig. 4. The mechanism of the reaction is therefore very similar as that catalyzed by soluble acids. However, while for homogeneously catalyzed reactions the concentration of the reactant in free solutions is important, the rate of ion exchanger catalyzed reaction is determined by the reactant concentration inside the swollen gel cavities. In the absence of a specific affinity between the reactant molecules and the ion exchanger gel, the reactant concentration inside the gel cavities is lower than in the free solution, due to the steric exclusion depending on the local density of polymer chains and the size of the reactant molecules.

The lowering of the reactant concentration due to steric hindrance of the polymer chains is the main cause of the difference between the reaction rates in the presence of an ion exchanger and a soluble acid of comparable strength, respectively. This has been proved in the hydrolysis of saccharose by the quantitative correlation of the catalytic activity of a wide series of ion exchanger catalysts and the steric effects as predicted from the swollen-state morphology of the catalysts characterized by means of ISEC [62]. In specific cases the steric effects of the polymer backbone can be mitigated by influences of the chemical nature of the polymer gel. For example, in the case of the hydrolysis of ethylacetate, ion exchanger catalyst may be more effective than a soluble acid due to preferential absorption of ethylacetate into ion exchanger

gel [105]. Nevertheless, even in this case the steric effects of the polymer chains play a dominant role and an increase of the cross-linking of the polymer matrix brings diminishing of the reaction rate in the same manner like in absence of the preferential absorption.

However, most of the industrial processes using ion exchanger catalysts proceed in the non-aqueous environment or in solutions with very low water concentrations. Reactants are there protonated by the undissociated sulfonic groups. Polymer chains to which are functional groups bonded are no more a steric hindrance only, the reaction proceeds in direct contact with them, with an adsorption of the reactant on the chain, by a mechanism similar to the conventional heterogeneous catalysis (see the schematic depiction in Fig. 5).

The most important commercial process catalyzed by a OCPs is the production of methyl *t*-butyl ether (MTBE). MTBE is an excellent substitute of alkyl-lead derivatives as an anti-knock agent in gasoline. Moreover, it allows a dramatic reduction of the level of carbon monoxide in the exhausts released by cars equipped with catalytic converters [106]. These circumstances have boosted the demand of this commodity and the world-wide production capacity on stream had increased from 1.5×10^5 t/year in 1978 to 13×10^6 t/year in 1994 and in the year 1998 it increased up to 20×10^6 t/year. Recently, there appeared pressure to phase-out its application as the fuel additive, due to the increasing problems with water pollution stemming from relatively good solubility of MTBE

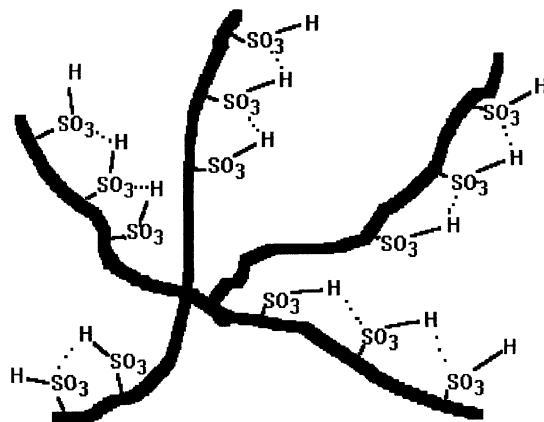


Fig. 5. Undissociated acidic groups bonded to the polymer chains of ion exchanger catalysts in non-aqueous environment.

in water [107]. MTBE is commercially produced by the acid catalyzed addition of methanol to isobutene.

The acid catalyst is a sulfonated S/DVB ion-exchange resin. The process has been developed by Italian researchers [108] from Snamprogetti/Ecofuel (formerly ANIC) in the late 1960s. The first commercial plant was built in Ravenna and went into operation in 1973, with a production capacity of 10^5 t/year. Since then a number of processes have been developed and practiced by other companies, such as Hüls, Arco, CD-Tech [58]. The catalysts employed in the industrial practice are macroporous cation-exchange resins, such as Amberlyst[®] 15 or Lewatit[®] SPC 118. Their surface area is 40–50 m²/g and the content of sulfonic acid groups is about 4.8 mmol/g (based on dry material).

In the relevant literature it is frequently stated that the macroporous morphology of the resin catalyst is needed because a microporous morphology would have produced unacceptable diffusional limitations in the MTBE synthesis. However, this is not quite true especially as a general statement. In fact, comparative tests of the activity of ion exchanger catalysts with widely differing morphology, carried out at conditions corresponding to the start of the process [109], did show that even gel-type resin catalyst had activity comparable with that of the macroporous ones. Moreover, one catalyst with an exceptionally high BET surface area exhibited in fact the lowest activity (Table 3). Apparently, the reaction proceeds predominantly inside the swollen polymer gel matrix. In addition, only a slight, if any, dependence of the catalytic activity on the polymer skeleton morphology was found, which indicates that most of the acidic centers participating in this reaction have similar efficiency [109].

The steric effects of polymer chains, which are crucial in aqueous environment (see above), seem to be much less important in the non-aqueous reaction

environment of MTBE synthesis. It has been proposed that the liquid-phase synthesis of MTBE on ion exchange resins proceeds quasi-homogeneously in “excess” of methanol $\text{Me}_2\text{C}=\text{CH}_2/\text{MeOH} < 1.7$, mol/mol) and quasi-heterogeneously at low methanol content [110,111]. In the former case the mechanism is ionic and the rate-determining step is the formation of carbenium ions by electrophilic attack of protonated methanol molecules, formed in the liquid phase, to the olefin. In the latter case a concerted proton transfer, which involves adsorbed reactant molecules, occurs [112].

According to a recent re-evaluation of the reaction, which takes into account the non-ideality of the liquid phase [113], the MTBE synthesis is proposed to be a quasi-heterogeneous process altogether. Therefore, the reacting molecules are always protonated by catalytic centers, which are part of the polymer chain. Accordingly, enthalpic interactions due to chemisorption on active centers become also important in the penetration of reactants into the swollen polymer gel, and the resulting attractive force outweighs the steric exclusion effect, which prevails in aqueous environments. For relatively small molecules like methanol, isobutylene or MTBE only a negligible proportion of active centers is completely inaccessible, even in the most cross-linked and least swollen resins. As a result, the intrinsic activity of acidic centers for MTBE synthesis is practically independent of the local morphology of the polymer carrier, at least at the initial stages of the reaction, when the methanol concentration in the reaction mixture is still relatively high [114,115].

On the other hand, as it was stressed above, a remarkable characteristic of OCPs is the dependence of their properties on the nature and composition of the reaction environment. During MTBE synthesis the change in the polarity of the reaction environment is quite significant, as the goal is to convert

Table 3

Properties of the examined ion exchangers and their catalytic activities in the MTBE synthesis^a

Trade name	Type	BET surface (m ² /g)	Reaction rate (mol/g h)
Lewatit [®] SC 108	Gel	0	0.73
Lewatit [®] SPC 108	Macroporous	15	0.81
Lewatit [®] SPC 118	Macroporous	45	0.80
Amberlyst [®] XN1010	Macroporous	580	0.31

^a 70°C; mol ratio of isobutylene and methanol 1:1; CSTR reactor; conversion approx. 7%.

all methanol into MTBE and in the last stages of the process the reaction mixture consists of nearly non-polar components only. Therefore, substantial changes in the reaction mechanism and selectivity are to be expected. Rehfinger and Hoffmann [111] described these changes in terms of macropore diffusion of methanol as the rate-controlling step. Diffusional effects in this reaction were detected also by other authors [116–118]. However, it is necessary to take into account also the catalyst morphology changes due to de-swelling induced by methanol disappearance from the reaction mixture. Further research in this direction is required.

Mechanism of ion exchanger catalyzed reactions in non-aqueous environment is similar to that operating on conventional heterogeneous catalysts (adsorption–surface reaction–desorption). Kinetics of ion exchanger catalyzed reactions in non-aqueous environment, like MTBE synthesis is usually described with Langmuir–Hinshelwood equations constructed on the supposition of participation of more than one acidic center in the rate determining step [113]. Interpretation of the participation of more than one center could be done in various ways, e.g. by assuming a multicentre adsorption of reacting molecules [105,114,115,119–122] or by the higher acidity of a certain grouping of sulfonic groups compared with an isolated acid center [112,123]. Regardless of the interpretation, important consequence of the catalysis by a multiplet of sulfonic groups is more-than-proportional dependence of the reaction rate on the concentration of the acidic centers. In studies of ion exchanger catalyzed reaction in non-aqueous environment, where the concentration of the acidic centers was controlled by partial neutralization of the sulfonic groups with metal ions, a very steep dependence of the reaction rate on the degree of neutralization has been observed (e.g. [104,119,120]). This effect is especially unpleasant for deactivation of ion exchanger catalysts in industrial processes. Even small amount of cationic impurities in the process stream can diminish the catalyst efficiency quite substantially. However, it also indicates that an increase of the local concentration of the active centers above the limit of the conventional sulfonation of styrenic resins, that is one sulfonic group per benzene ring, could boost the catalyst activity more than proportionally to the increase of the exchange capacity. This approach has been used by

a few leading manufactures of ion exchangers who introduced a new generation ion exchanger catalysts designated for synthesis of MTBE: Amberlyst 35 (Rohm and Haas Co., USA), Purolite CT-175 (The Purolite Co., USA), Bayer OC-1501 (Bayer A.G., Germany). The manufacturer's information and a few papers in the open literature [124–127] claim that these catalysts could give in the MTBE or TAME synthesis significantly higher conversion and liquid hourly space yields than the ion exchange resins so far used for this purpose, like Amberlyst[®] 15 (Rohm and Haas Co., USA) or Lewatit[®] SPC-118 (Bayer A.G., Germany). Official information about substance of their special properties is rather scarce, but analyses of these resin show that they are indeed “hypersulfonated” [128].

5.1. Industrial synthesis of bisphenol A

Bisphenol A (2,2-bis(4'-hydroxyphenyl) propane) is an important intermediate in the production of polycarbonates and epoxy resins. Its manufacture by condensation of acetone and phenol is catalyzed by a gel-type strongly acidic resin and, after the production of motor fuel additives like MTBE, it is probably the second largest industrial process using an OCP-based catalyst (ca. 800,000 t/year in USA [129]). Both the reaction rate and selectivity of the acid catalyzed synthesis of bisphenol A is promoted by the presence of mercaptanes in the reaction environment. Resin catalysts industrially used for this process are noteworthy because they carry both the acidic centers and the promoting mercapto-groups introduced upon partial neutralization of the sulfonic acid groups with cysteamine (2-mercapto ethyl amine).

This catalyst is an elegant example of how the resin chemistry allows the tailoring of the catalyst for specific reaction needs. However, the introduction of the second functionality occurs at the expenses of the overall number of acidic centers and, therefore, one must compromise between activity and selectivity and this example illustrates how the concentration of active centers in a OCP can influence the final performance. Fig. 6 depicts the dependence of the relative catalytic activity of ion exchanger catalyst for the bisphenol A synthesis on the fraction (F) of the sulfonic groups in the catalyst neutralized with cysteamine [130].

The relative catalytic activities are referenced to the highest activity attainable with the unpromoted

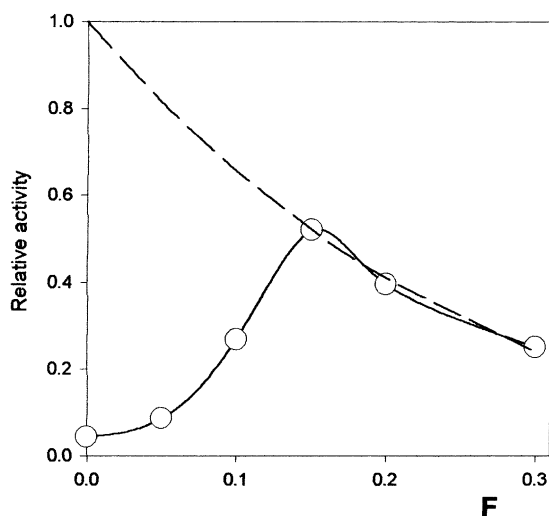


Fig. 6. Dependence of the relative activity of the cysteamine-modified ion exchanger catalyst of the synthesis of bisphenol A on the fraction of the acidic groups in the catalysts neutralized with cysteamine (F). Unit relative activity corresponds to the combination of the ion exchanger catalysts with the homogeneous promoter (ethylmercaptan) dissolved in the reaction mixture. For the description of the lines see the text.

heterogeneous ion exchanger catalyst in the presence of ethylmercaptan as the homogeneous promoter (relative activity = 1) under otherwise identical conditions. The relative activity (solid line) goes through a maximum at $F = 0.15$. At higher F values the promoting effect cannot be enhanced any more and further increase of the mercapto group concentration only lowers the concentration of the acidic centers. Kinetic study [131] suggests that the activity of the ion exchanger catalysts of the bisphenol A synthesis is proportional to the fourth power of the acidic sites concentration, as shown by the dotted curve in Fig. 6. This is the reason why the bifunctional catalyst, in

which the immobilization of the second functionality is achieved at the expenses of the concentration of the acidic sites, can reach only about half of the activity of the unmodified resin catalyst used together with the homogenous promoter dissolved in the reaction mixture. Nevertheless, this is a reasonable price to be paid for the replacement of the difficult-to-handle mercaptan promoter with a fully heterogenized catalyst making design and operation of the bisphenol A manufacture much more simple.

The reaction rate in the synthesis of bisphenol A is strongly influenced by the microenvironment of the swollen gel matrix in the immediate vicinity of the active centers [132]. As far as the catalytic activity alone is concerned, the more swollen (less cross-linked) the polymer mass is, the better. However, in industrial applications it is necessary to take into account that extensive swelling of the polymer matrix adversely influences the mechanical properties of the catalyst and reduces the efficiency per unit of volume of the catalyst bed. A good illustration of differences between various types of ion exchangers give results of comparative tests of a series of commercially resin catalysts available from Bayer A.G., Leverkusen, Germany (Table 4) [133]. The catalysts are designated Lewatit[®]-SC (gel-types) or Lewatit[®]-SPC (macroreticular types) and represent practically the whole spectrum of the strongly acidic resin catalysts commercially available. For the test all resins were modified by neutralization of 15% of acidic groups by cysteamine.

The volume of the water-swollen resins is important for practical applications because the catalyst is usually charged and discharged from the reactor in this state. The results of the activity tests are then shown both per mass of the dry resin and per volume of the wet catalyst. The first set of data shows the “absolute”

Table 4
Comparison of various Lewatit[®] ion exchange resins as catalysts for bisphenol A synthesis^a

Lewatit [®] type	SC-102	SC-104	SC-108	SPC-108	SPC-118
DVB content (%)	2	4	8	8	18
Swelling volume (cm ³ /g) ^b	8.1	4.1	2.4	3.9	3.3
Reaction rate (mmol/g h)	27.4	23.9	3.5	25.1	11.4
Reaction rate (mmol/cm ³ h)	3.4	5.8	1.4	6.4	3.4

^a 70°C; acetone-phenol mol ratio 1:8; CSTR reactor; acetone conversions 5–10%.

^b In water.

efficiency of the resin while the second gives a measure of practically attainable performance in industrial reactor.

The highest catalytic activity per gram of the dry resin is exhibited by the lowest cross-linked ion exchanger Lewatit[®] SC-102. However, this resin has also the highest water-swollen volume and hence, its activity per unit of reactor volume (last line of Table 4) is rather low. On the other hand, the least swollen resin Lewatit[®] SC-108 offers in the catalytic reaction environment too sterically crowded and therefore, both per unit of mass and unit of volume, this resin is the worst catalyst. From point of view of the optimal use of the reaction volume, the Lewatit[®] SC-104 and Lewatit[®] SPC-108 give the best performance.

6. Conclusion

Functional synthetic resins serve as efficient industrial heterogeneous catalysts and are promising supports for the development of new types of supported catalysts (including supported metal catalysts), potentially useful in the industrial area of fine chemicals synthesis. They offer an environment for the catalytic reaction quite different from that of a free solution or the surface of conventional heterogeneous catalysts based on inorganic supports. In this connection, the microenvironment of a catalytic site embedded in the polymer network can almost be considered as a microreactor. In principle, it can be designed and “constructed” on the basis of a sort of molecular engineering approach. However, we are still far from a full understanding of the details of the “polymer gel reactors” at the molecular level. For a full exploitation of their potential it will be necessary to gather as much as possible information on the physical chemistry of the swollen polymer networks. In this review we have presented some approaches and methods, which can help in this connection, but our knowledge is still limited and further efforts to this end are highly desirable.

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