Macromol. Symp. ***2001,*** *164, 443-456*

Bifunctional Catalysts Supported on Polymers for the Preparation of Bisphenol A

*André Revillon**[1], *Eric Puccilli*[1], *Isabelle Guibert*[2], *Alain Guyot*[1]
[1]CNRS-LMOPS, BP 24, F-69390 Vernaison, fax 33/(0)4 78 02 77 38
[2]Rhône-Poulenc, CRC, BP 62, F-69192 Saint-Fons cedex, France

SUMMARY: This work is relative to attempts for obtaining acid-thiol supported polymers that may be used as solid bifunctional catalysts, active in the Bisphenol A synthesis. Five approaches are tested with modified sulphonic styrene-based polymers obtained either by multi-polymerisation in one or several steps and derivatization. The objective is to get simultaneously sufficient capacity and high selectivity, by using an adequate acid/thiol ratio, and enhanced sites accessibility via an optimisation of the morphology. Reactivity results are favourably compared to those obtained in a homogeneous process.

Introduction

The product. 2,2-Bis(4'-hydroxyphenyl) propane, known as Bisphenol A (BPA), is an important starting material used in ignifugation materials and various polymers, namely epoxy and polycarbonates. It is obtained by acid catalysed condensation of phenol (in a large excess) and acetone. Among the Bronstedt acids, hydrochloric acid is the preferred one in the homogenous process at 80°C. Chlorinated compounds are used as solvent. Unfortunately, the desired p,p' isomer is accompanied by side products (Figure 1). Yet, the selectivity is enhanced by the action of a nucleophilic co-catalyst, which is generally a sulphur compound (organic or inorganic), preferentially a thiol or a dihydroxybenzene, e.g. resorcinol.

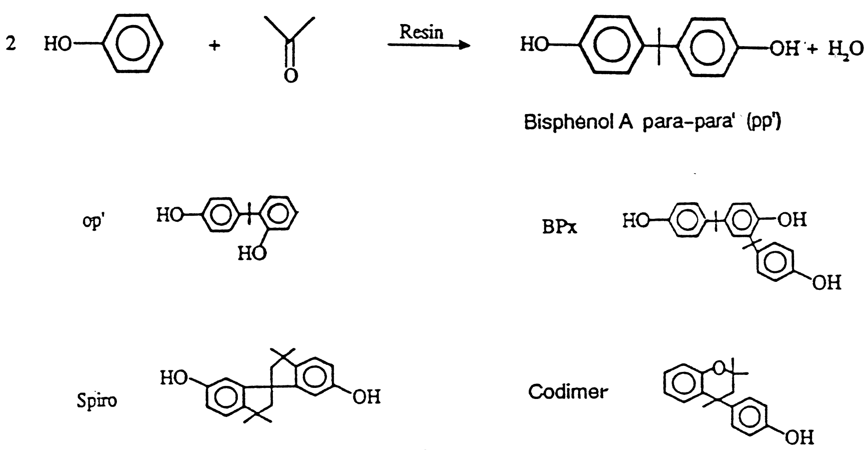

Fig.1. Conversion into Bisphenol A and by-products

CCC 1022-1360/00/$ 17.50+.50/0

Supported catalysts. In order to lower environment damage and corrosion problems, as well as to benefit of advantages of heterogeneous processes (easy separation of components, recycling of catalysts and recovering of reagents), ion exchangers are used. Catalysts are of strong acid type, with sulphuric groups, a part of them being neutralized by a mercaptoamine, generally thioethanolamine (TEA), e.g. (1). The difficulties are to obtain simultaneously a high enough acid capacity and a correct acid on thiol ratio. Ways to introduce a SH group on the polymers may be found in (2-4). Patents appeared in 1957 (UC, improved in 1966: enhancement of conversion from 52% to 75% in presence of SH), and were rapidly improved (Hercules, 1960: Dowex 50wx4 with 3.5 SO_3H and 1 meq/g SH). In spite of their interest, classical organic resins have inherent problems: limited thermal stability and poor mechanical properties. They also suffer of diffusion control, due to their swellability. Our approach has consisted in improvement of mechanical properties and site accessibility by supporting the functional polymers on an organic optimised core.

This work. Recently, we have shown that active site accessibility of styrene based networks is enhanced by functionalization of cross-linked polymers prepared in a two-step process (5). Moreover, the possibility of the choice of a proper site environment may increase the selectivity. Difficulties are i) to obtain a high ratio of graft to free polymer in order to give a sufficiently high capacity, which favours high yield in the catalysed reaction and ii) to combine lipophily of supports to hydrophily of sites.

Functional polymers may be obtained either by polymerisation of a functional monomer or by derivatization of a polymer; these possibilities are multiplied in the case of bifunctional products. Vinylbenzyl chloride (VBC) is largely used as a precursor, but styrene sulphonyl chloride (SSC) and potassium or sodium styrene sulphonate (SSK and SSNa) are other functional candidates (6, 7) with large possibilities. So we have considered five pathways (b to f) to obtain these styrene-based sulphonic catalysts. They are based either on the free-radical terpolymerisation of two functional monomers, which are precursors of acid and thiol groups, in presence of a cross-linker or are modifications of a cross-linked co- or ter-polymer. This may be obtained either by free-radical post-copolymerisation of one of the functional monomers or its precursor, or by reaction with a small molecule. When a thiol is present, this one may be used as a tool to generate new polymer chains and modify some sites. Yet, its chain transfer behaviour affects chain length and polymer yield.

Experimental

a-Polymer matrix

The polymer matrix is a crosslinked styrene-divinylbenzene copolymer (S-DVB) obtained by a free-radical suspension process, in presence of a polymer porogen (MW 250000 g/mol polystyrene in toluene solution); Arabic gum is the protective colloid and ammoniac salt of a styrene-maleic acid copolymer (SMA) is added as dispersant. After 5-8 hours of polymerisation (~80°C) under stirring, beads are filtered, washed, extracted with toluene in a Soxhlet and finally, dried at 60°C for 24 hours under vacuum. Porogen is given as weight fraction of the total organic phase; %PS is the weight fraction of polystyrene in the whole porogen phase. Varying these different amounts and ratios affords to monitor pore volume and pore size distribution. High amounts of DVB lead to a permanent porosity and a good mechanical stability. High contents of porogen (polystyrene in toluene) lead to highly porous networks (5). Vinylbenzyl chloride (VBC) or styrene sulphonyl chloride (SSC) may be added under the same conditions, as a third monomer. They may be derived further. Another way is to post-polymerise the third monomer with the residual VBC double bonds of the matrix: this leads to a different morphology, with more mobility of the grafted polymer chain and increased accessibility of the active sites. Composition of reaction media and pore volume of the matrix are given in Table 1.

Table 1. S-DVB macroporous networks. Composition and porosity

Resin	% poro	% PS	% DVB	V_p cm^3/g
Q8	60	15.0	20	1.00
332	55	10.0	30	0.46
331	50	10.0	30	0.10
P8	60	5.6	30	0.13
333	65	10.0	30	0.65
341	65	12.0	30	0.70

Final reactive polymers, which are the bifunctional catalysts, are obtained by one of these five ways:

b-Modification of a thiol copolymer by polymerising SSK or SSNa

c-Post-copolymerisation of VBC on a S-DVB matrix, sulphonation and derivatization

d-Post-copolymerisation of SSC on S-DVB resin and hydrolysis

e-Terpolymerisation of S-VBC-DVB and sulphonation

f-Terpolymerisation of VBC-DVB with SSC and derivatization

b-Modification of a thiol copolymer by polymerising potassium or sodium styrene sulphonate

Principle is to use the very reactive thiol groups present on the matrix to act as chain transfer agents versus the added monomer for grafting a part of the new polymer chains. A commercial thiol resin (Duolite IMAC GT 73, Rohm & Haas, 2 or 0.6 meq/g thiol capacity) is swollen up to 24 hours in an aqueous solution of sodium or potassium styrene sulphonate; potassium persulphate as initiator is added when the desired temperature (50°C to 80°C) is reached. Various concentrations, reagent ratios and reaction times are recorded in Table 2. After reaction, the resin is washed with water, then with diluted hydrochloric acid and again with water, before drying for 24 hours, under vacuum, at 50°C. The non-grafted polymer is water soluble and extracted from washing solutions; it is purified by precipitation in methanol, filtration and drying in the same way as the grafted one.

Table 2. Polymerisation of a styrene sulphonate salt (SS K or Na) on a thiol resin

Final resin (metal)	Thiol resin, g	Mon SSS mol/l	persulph. mmol/l	H_2O g	pH	swelling, h	reaction, h	T°C
Na2	8.0	0.6	3.7	222	7	18	18	60
Na3	8.0	0.5	6.8	122	7	24	20	80
Na4	8.0	0.6	3.7	222	7	24	20	80
K1	5.0	1.0	14.0	38	13	18	18	60
K5	8.0	0.9	6.5	62	13	24	63	60
K6	5.0	0.5	2.7	75	13	1.5	20	60
K7	4.3	3.2	19.0	11	13	0	65	50
K8	2.6	3.2	60.0	19	1	0	22	50
K9	3.0	2.4	48.0	19	1	0	19	50
K10	3.0	2.5	24.0	16/4(a)	13	1	17	70

(a): water 16 g, toluene 4 g, in presence of tris(2-(methoxyethoxy)ethyl)amine

Table 3. Results of styrene sulphonate salt (SSS) polymerisation on a thiol resin

Resin	conv %	graft/ free	total H^+ meq/g	H^+gr theo meq/g	H^+gr eff meq/g
Na2	84	0.01	0.7	0	0.1
Na3	57	0.09	0.9	0.4	0.3
Na4	83	0.02	0.2	0	0.2
K1	54	0.15	1.2	0.5	0.7
K5	81	0.26	1.4	1.1	0.9
K6	78	0.10	1.0	0.5	0.4
K7	73	0.28	1.6	1.2	1.1
K8	85	0.07	1.7	1.2	1.2
K9	82	0.13	1.7	1.2	1.2
K10	63	0.13	1.7	1.3	1.2

Final material is weighted to determine quantity of grafted polymer and acid content, which is compared to that measured by titration and elementary analysis. Infra-red spectra allow identification of thiol and sulphonic salt and acid bands at 2580 cm^{-1} and 1180-1130 cm^{-1}, respectively. Polymerisation results are given in Table 3, conversion and selectivity in Table 4.

Table 4. Conversion and selectivity of SS Salts (Na and K) polymers for Bisphenol A synthesis

Resin	R % BPA	R % BPX	codimers %	Q = op'/op'+pp'
ref	32.0	.....	.....	0.132
Na2	0.9	.....	.....	0.222
Na3	19.1	0.26	1.8	0.182
Na4	24.2	0.44	2.5	0.184
K1	17.5	0.20	1.1	0.174
K5	2.7	.....	.....	0.111
K6	10.7	.....	1.1	0.185
K7	32.2	0.40	2.5	0.161
K8	36.0	.....	3.1	0.164
K9	30.5	.....	2.4	0.167

Table 5. VBC Grafting conditions for the post-copolymerisation on S-DVB resins

Resin	g	AIBN mmol/l	VBC mol/l	solvent cm^3	% Δw	T°C	Time, h	Cl meq/g
ST900C	4.2	23.0	4.2	tol, 4	2.5	85	2	0.3
341C	5.3	75.4	4.9	tol, 4	112.0	85	2	3.8
333C	6.2	16.5	1.6	hept, 30	81.3	85	20	2.9
332C	13.7	37.6	3.5	DCE,15	27.3	85	20	1.5
Q8C	8.2	38.3	4.0	DCE,10	35.1	85	24	1.8
331C	5.8	60.4	3.7	DCE,10	35.9	80	2.5	1.8
P8C2	24.5	76.0	3.8	DCE,50	43.7	80	3	2.1

c-Post-copolymerisation of VBC on a S-DVB matrix, sulphonation and derivatization

In the first step a macroporous resin is obtained. Polymerised DVB has some residual double bonds at the surface. These ones are copolymerised in a second step with VBC. For that, resin is allowed to swell in VBC diluted with toluene, heptane or 1,2-dichloroethane (DCE), for 3 days. Then, AIBN, deionised and degassed water are added and temperature is raised to 80°C-85°C for 2 to 24 hours. Finally, the resin is filtered, washed under refluxing toluene to remove free polymer, then washed with methanol and dried under vacuum at 50°C. Condition parameters are given in Table 5. A reasonably high content in VBC is obtained.

Then this product is sulphonated either with chlorosulphonic acid or sulphuric acid, under the conditions shown in Table 6. In the first case (chlorosulphonic acid), after swelling the resin in

$CHCl_3$ (TCM), reaction is performed either at temperature 20°C or at 65°C for several hours, by drop-wise addition of chlorosulphonic acid, under stirring. Excess of acid is neutralized by methanol; the resin is filtered, washed with water and methanol and dried under vacuum.

Table 6. Sulphonation conditions for VBC-S-DVB resins and resulting capacity

Resin	g	solvent cm^3	sulph cm^3	T°C	Time, h	% Δw	meq H^+/g	meq Cl/g before and after
PSCl26S1	4.9	TCM, 90	C, 3	20	1.5	12.9	0.4	.....
PSCl26S2	4.4	TCM, 90	C, 7	65	4	9.3	0	.....
341CS1	5.2	TCE, 60	S, 5	60	17	0.7	...	.....
333CS1	4.4	TCE, 60	S, 5	70	1	2.2	...	.....
PSCl26S3	4.2	DCE, 10	S, 15	80	5.5	18.9	0	.....
333CS2	3.0	DCE, 5	S, 50	80	0.5	24.1	2.4	2.9-0-7
333CS3	2.7	DCE, 10	S, 50	80	0.8	26.9	2.7	2.9-0.5
333CS4	1.0	DCE, 5	S, 50	87	1.5	20.3	3.1	2.9-0.4
341CS2	2.3	DCE, 5	S, 60	82	1.5	20.3	2.6	
331CS	4.0	DCE, 20	S, 70	80	0.8	34.5	3.4	1.8-0.2
332CS	3.6	DCE, 25	S, 65	80	0.8	45.1	3.7	1.4-0.2
P8C1S	4.1	DCE, 20	S, 70	80	0.8	31.2	2.9	2.1-0.4
Q8CS	3.7	DCE, 30	S, 70	80	0.8	48.7	3.9	1.8-0.5
P8C2S	17.4	DCE, 85	S, 150	85	0.5	23.0	2.3	.....-0.1

C (in the sulph column) means $ClSO_3H$ and S is for H_2SO_4

Table 7. Composition in H^+ and SH functions of resins. Values of conversion and selectivity in phenol-acetone condensation

Resin	H^+/SH	H^+ meq/g	R % BPA	R % BPX	R % codim	Q = op'/op'+pp'
reference[a]	82-18	3.8	66.2	0.4	0	0.033
P8C1ST	87-13	2.0	49.1	05	0.6	0.065
P8C2ST1	74-26	1.4	32.0	0.3	0.2	0.056
P8C2ST2	70-30	1.6	34.0	0.3	0.3	0.060
331CST	89-11	2.5	30.3	0.2	1.2	0.103
332CST	96-04	2.5	28.4	0.2	2.7	0.141
Q8CST	100-0	3.1	28.4	0.2	2.8	0.146
SSK8	.....	1.8	36.0	.....	3.1	0.164

[a] ref: Dowex 50WX8/TEA, molar ratio 82/18

In the second case, sulphuric acid (5 to 150 cm^3) is heated to 60°C-85°C; 3-5 g of swollen resin in 1,2-dichloroethane (5-85 cm^3) or 1,1,1-trichlorethane (TCE) is added as well as acetic anhydride (1 cm^3) to limit additional cross-linking. After 30 min, the resin is filtered, washed with water and methanol and dried under vacuum.

Acid content is measured and elementary analysis gives sulphur content as well as residual Cl. Final step is substitution of Cl by SH, by means of thiourea and further alkaline hydrolysis. 3 g of thiourea are added to 5 g resin (2 meq Cl/g) in THF-ethanol mixture (70-30 cm^3). Reaction takes place at 80°C for 2 days, under stirring. Then the resin is filtered, washed with water, then THF and toluene. To this resin in 60 cm^3 toluene, an amount of 0.1 g tetrabutyl ammonium iodide in a concentrated soda solution (4 cm^3) is added. The mixture is heated at 80°C for 2 days under N_2. The resin is filtered, washed with THF, water, THF/HCl 6N (3/1), water, THF, acetone, DCE and finally with methanol, then dried under vacuum. Compositions and results in Bisphenol A synthesis are given in Table 7.

d-Post-copolymerisation of SSC on S-DVB resin and hydrolysis

SSC was prepared according to ref 6. The S-DVB resin is swollen in toluene or DCE and SSC is added. At the chosen temperature AIBN is allowed to initiate the reaction, which is carried out for 16 hours. Then, the modified resin is washed with THF and hydrolysed with water at 50°C. Finally thioethanolamine converts a part of acid groups in thiol groups. Conditions and results are shown in Table 8. Wide IR bands at 1200 cm^{-1} are attributed to sulphonic groups.

Table 8. SSC Polymerisation on S-DVB resin

Resin	g	SSC mol/l	Solvant cm^3	T °C	AIBN mmol/l	Time, h	H^+theo meq/g	H^+eff meq/g
341	5.5	3.4	tol, 6	80	80	16	1.3	0.5
P8	4.9	3.6	DCE, 9	60	60	16	2.5	1.6

ref: Dowex 50WX8; ref/SH: Dowex 50WX8/TEA at molar ratio 82:18

e-Terpolymerisation of S-VBC-DVB and sulphonation

As indicated in *a*, styrene, vinylbenzyl chloride and divinyl benzene are polymerised in suspension in presence of a polystyrene solution in toluene as a polymer porogen.

Table 9. Synthesis and composition of sulphonated S-DVB-VBC terpolymers

Resin	g	DCE cm^3	T°C	time h	H^+ meq/g	SH meq/g	H^+final meq/g
456S2	5.5	10	80	0.8	1.8	0.8	1.2
456S3	7.2	30	85	1.2	2.0	0.6	1.6
456S4	3.5	30	85	2.5	3.1	0.4	2.5

Sulphonation mode by sulphuric acid (80cm^3) and thiol derivatization are similar to those described in (c). Conditions (composition of polymers) and results (conversion in Bisphenol A) are given in Tables 9-10. On IR-spectra are shown thiol band at 2550 cm^{-1}, SO_2 bands at 1130-1180 2550 cm^{-1} and sulphonic acid band at 1250 cm^{-1}.

Table 10. Composition of resins. Conversion and selectivity in Bisphenol A synthesis

Resin	H^+/SH	R% BPA	R% BPX	% codim	Q = op'/op'+pp'
ref	100-0	32	....	3	0.130
ref/SH	82-18	59	0.2	0	0.031
P8C1ST	87-13	42	....	1	0.077
456S2	60-40	23	0.1	..	0.049
456S3	72-28	53	0.5	0.2	0.051
456S4	86-14	41	0.2	..	0.065

Table 11. Terpolymerisation SSC-DVB-VBC (method f)

Resin	SSC mol/l	DVB mol/l	VBC mol/l	poro % in org	%PS in poro	Initiat. mmol/l	Arab Gum g	SMA cm^3	H_2O cm^3	NaCl g	T° C	Stir. rpm
PE1	1.4	0.23	0	61.6	21.4	A, 19	6	7	250	90	65	300
PE2	1.0	0.10	0	63.5	16.4	A, 25	8	9	400	140	60	200
PE3	1.2	0.41	0	60.3	20.5	BP 18	4	5	120	8	85	250
PE4	1.4	0.62	0	47.5	14.3	A, 58	5	5	70		80	110
PE5	1.2	0.60	0	50.3	20.0	C, 23	7	8	120	24	60	200
PE6	1.0	0.40	0.38	56.2	25.0	C, 22	5	5	60	6	56	280
PE7	1.0	0.22	0	63.5	12.8	C, 15	5	6	80	20	56	180
PE8	0.9	0.46	0.26	57.4	14.3	C, 12	4	5	80	20	60	210

Initiator: A=AIBN; BP=benzoyl peroxide; C=hexadecylpercarbonate

f-Terpolymerisation of VBC-DVB with SSC and derivatization

The classical suspension process has been adapted to the VBC-DVB-SSC terpolymerisation by dissolving 6 g NaCl and Arabic gum (protective colloid) in deionised and degassed water (60 cm^3), heating at 56°C, then adding a mixture of the three monomers (for instance, 14.1 g SSC, 7.6 g DVB, 4.1 g VBC), a porogen solution (30 g toluene, 10 g polystyrene MW 250000 g/mol) and 0.9 g hexadecyl perdicarbonate as initiator. Porogen is expressed in weight fraction of the total organic phase; %PS is the weight fraction of polystyrene in the whole porogen phase. Varying these quantities allows monitoring pore volume and pore size distribution. Other conditions are given in Table 11. After 3 min, the ammoniac salt of a styrene-maleic acid copolymer (SMA) is added as dispersant. After 30 min, beads are formed. A constant stirring rate (e.g. 280 rpm) is maintained throughout the reaction. After 5 hours of polymerisation, beads are filtered and washed with THF at 50°C, then hydrolysed at different temperatures for one hour in a 2N soda solution. Substitution of Cl by SH is performed by thiourea, as described in (c). Other reaction conditions and the composition are shown in Table 11.

g-Conversion into Bisphenol A in the presence of the bifunctional catalysts

The functional resin is poured into a stirred reactor and a mixture of phenol and acetone (8:1) is added; temperature is kept at 80°C for 6 hours. Liquid chromatography (reverse phase, with H_2O-CH_3CN as mobile phase) is used for kinetic and composition analysis. An example of separation of Bisphenol A and isomers is given in Figure 2. Conversion into Bisphenol A (BPA) is expressed as R% BPA. Side products are BPx and codimers. Q = op'/(op'+pp') is a measure of selectivity: the lower Q, the higher the selectivity in BPA isomer.

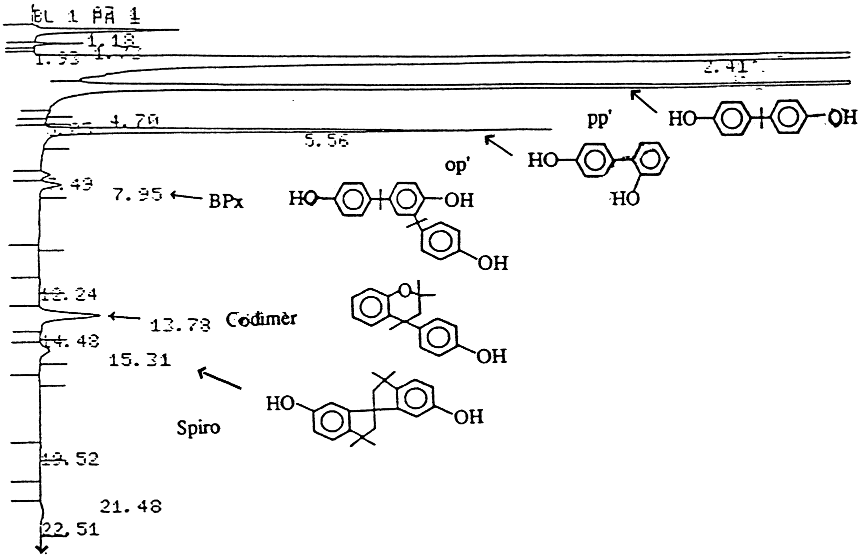

Fig.2. Reverse phase liquid chromatography analysis of a reaction mixture

Results

Process b-Styrene sulphonate salts grafted on a thiol resin.

The first interest of this approach is a technical one and lies in its ease, since this is a one-step process. The second interest is a scientific one, since changing the extent of polymerisation allows to monitor the respective amounts of thiol and acid. In this process, we have observed a large increase of the capacity by increasing monomer and initiator concentrations and decreasing the water to resin ratio, corresponding to increase of polymerisation rate (Table 2, K8, K9). On the contrary, the increase of polymerisation rate with temperature (Na3, Na4) is accompanied by a corresponding decrease of chain length, so that the amount of grafted polymer decreases, as well as the ratio (g/f) of grafted to non-grafted (free) polymer. The hydrophilicity of the monomer favours the polymerisation outside the resin, so that the transfer efficiency is reduced. The effective acid capacities originated from grafting are not higher than 1.2 meq/g. Attempts to increase monomer lipophilicity by complexing the cation with a kryptant (tris(2-(methoxyethoxy)ethyl)amine) does not lead to an increase of grafted polymer (K10). The conversion is not total (maximum is 85%) in spite of the long reaction times (up to 65 h). High pH value enhances grafting, since the initiator decomposition rate is lowered and longer times favour the chain transfer. The disadvantage of persulphate is its oxidising ability versus thiol, so that potential capacity in thiol is decreased. Decrease of thiol concentration induces reduction of chain transfer and of final acid concentration. The whole conversion is similar for sodium and potassium salts, but SSK leads to higher grafted capacities than the sodium salt (SSNa), which is less water-soluble. The yield could be improved by using an organo-soluble peroxide, in presence of a water-soluble solvent.

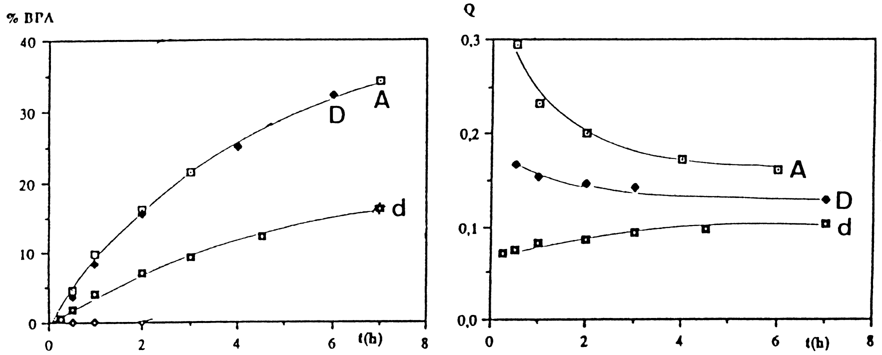

Fig.3. Conversion curves into BPA and Q values, in the presence of an acidic/thiol resin K7 (A) and two references catalysts, Dowex 50W/X8 (D) and Duolite ES 465 (d)

Conversion into Bisphenol A obeys a first order law. For example, rate constant is 8 10^{-5} s^{-1} in the presence of SSK7 or a reference resin. It is only one third of this value for Duolite ES465. Conversion with resin SSK8 is slightly higher (36%) than with a sulphonic commercial resin (32% with Dowex 50WX8) and selectivity is similar for the two catalysts, respectively 0.164 and 0.132: lower are Q and codimers, better is pp' conversion (Table 4). SSK8 has certainly relatively short chains that are in the outer part of the resin (no swelling, high amount of initiator). For some other resins (SSK7 and 9), the conversion is reasonable (32%), decreasing with capacity (for SSNa4, 24%). This is insufficient, partly due to the low capacity (around 0.8 meq/g), oxidation of thiol groups and low selectivity.

Process c-Sulphonic and thiol groups derived from VBC copolymers, on S-DVB matrix

The first step of the grafting of VBC on the resin is efficient, leading up to 3.8 meq Cl/g; it does not depend too much on reaction time, the nature of diluent for the initial swelling and the amounts of monomer and initiator (Table 5).

For the second step, $ClSO_3H$ does not allow an effective sulphonation. The observed weight increase is suspected to be due to sulfone bridge formation. In consequence, efforts were directed to the use of sulphuric acid. This leads to a capacity up to 3.7 meq H^+/g, when using a large acid excess, a highly porous resin and a good swelling diluent, such as DCE (Table 6). The initial sulphonation rate is sufficiently high to avoid long reaction times, which favour side reactions to occur progressively (chemical and physical degradation). The acid titration results agree with the results of the elemental analysis. An acid content higher than the molar VBC equivalent indicates that the matrix itself is sulphonated and not only the added rings resulting of the post-copolymerisation. The sulphonation is always accompanied with large dechlorination, so that the potential thiol amount is reduced.

The thiol group is obtained by substitution and HCl elimination. The conversion into SH is around 75%, but in some cases, the thiol amount is surprisingly higher than that of the precursor. Values of 0.5-0.7 meq/g are reasonable, for an acidity of 2 meq/g, if we consider that an adequate H^+/SH ratio is around 3-4. (Table 7).

A conversion into Bisphenol A as high as 50% is obtained, which is a better result than in the previous pathway. Similarly the selectivity is enhanced (lower Q, e.g. 0.06 instead of 0.15). But the results are better with a commercial acidic resin partially neutralized with thioethanolamine (Table 7).

The number of steps, and the decreased mechanical stability, as well as the difficult chemical control (sulphonation and proper derivatization) make this approach difficult, in spite of interesting reactivity results.

Process d-SSC grafting on S-DVB, with partial derivatization

This approach presents the advantage of grafting a lipophilic monomer on a lipophilic resin, the

SSC monomer being a precursor of acid group, which is easy to recover. Only preliminary results are indicated in Table 8. It appears that a moderate reaction temperature is preferable to obtain a reasonable acidity. Yet, it is inferior to the theoretical value (eg, 1.6 instead of 2.8 meq/g). Subsequent hydrolysis of SSC is almost complete, since residual Cl is only 0.1 meq/g. This monomer was used later in another way.

Process e-Terpolymerisation and derivatization in acid and thiol

A macroporous resin S-DVB containing VBC as a third comonomer, is modified in the same way as the postcopolymerised one (c). Good swelling in an excess of DCE allows to get 3.1 H^+/g. Yet, a decrease in Cl content when sulphonation extent increases is observed as previously (in b), so that the final derivatization in thiol leads to a moderate amount only (Table 9).

Table 12. Capacity of hydrolysed SSC-DVB-VBC resins (method f)

Resin	T°C hydrol.	S_{th} meq/g	S_{exp} meq/g	Cl_{th} meq/g	Cl_{exp} meq/g	H^+/g meq/g
PE1	....	4.1	....	4.1	....	....
PE1a	....	4.4	3.9	0	1.2	....
PE1b	....	4.4	4.0	0	0.5	....
PE5	....	2.8	....	2.8	....	....
PE5a	45	2.9	3.0	0	1.1	1.7
PE5b	65	2.9	3.1	0	0.6	1.7
PE5c	85	2.9	3.0	0	0.7	2.0
PE5d	100	2.9	3.1	0	0.2	2.3
PE6	....	2.6	....	3.8	3.2	1.8
PE6h	85	2.8	2.7	1.2	1.0	1.7-2
PE7	....	3.9	....	3.9	....	....
PE7h	100	4.2	3.9	0	0.2	3.2

The reactivity varies with the H^+/SH ratio as expected, observing a maximum for the value 72:28; this maximum corresponds also to an excellent selectivity (Table 10). Recycling tests have shown a slight decrease of reactivity.

Process f-Co- or Ter-polymerisation and derivatization in thiol

Instead of post-polymerising the acid precursor SSC, it was incorporated during matrix synthesis by copolymerisation with DVB. In some cases VBC has been added as the third monomer. Regular beads are difficult to obtain: they are accompanied of a powder, to an extent depending on the reaction parameters. Reaction at a constant stirring rate appears to be better than an increase of the rate after the gel sticking point. Expected and experimental S values are in agreement, which indicates similar reactivity of the monomers. Difficulty arises for hydrolysis (1h/NaOH), which needs high temperature and a basic medium (Table 12). Drying at 150°C does not alter the acidity. The resins with a CH_2Cl group may be successfully derivatized in thiol, and were tested when this amount was high enough. Table 13 allows comparison of the effect of thiol on conversion and selectivity. The better results are a conversion of 50% and a selectivity of 0.035, which are in the range of those obtained with a commercial resin in the presence of an added thiol-amine.

Table 13. Conversion for Bisphenol A synthesis and selectivity in the presence of terpolymers based on DVB-SSC-VBC

Resin	% R BPA	% R BPX	% codim	Q = op'/op'+pp'
ref	32	....	3	0.130
ref/SH	66	0.4	0	0.031
PE5d	5	....	0.1	0.069
PE7	38	0.7	....	0.035
PE6	50	0.4	0.3	0.060

ref: Dowex 50WX8 (4.9 meq/g); ref/SH: Dowex 50WX8/TEA, molar ratio 82:18

Conclusion

These various approaches for bifunctional acid-thiol resins synthesis, either by terpolymerisation or post-copolymerisation, or sulphonation and derivatization in thiol, have given interesting results. They indicate some ways for further development. Four of them, with an acid capacity in the range of 1.5-2 meq/g, lead to conversion into Bisphenol A, in the range of 50% and to a good selectivity (Q ratio about 0.055). These results (conversion) are better than those obtained with a commercial sulphonic resin (30% and Q, 0.16) and almost similar to those obtained with this reference material in presence of an added thiol (where Q is equal to 0.03). Optimisation concerns improvement of the capacity, control of the acid/thiol ratio and increase of the stability to prevent -SH departure during recycling tests.

References

1-K. Jerabek, Li G. Hun, K. Serinek, *Coll. Czech. Commun.*, **54**, 321-325 (1989)
2-M. Stern, M. Fridkin, A. Warshawsky, *J. Polym. Sci. : Polym. Chem. Ed.*, **20**, 1469-1487 (1982)
3-C-D S. Lee, W.H. Daly, *Adv. Polym. Sci.*, 61-90 (1974)
4-J.M.J. Fréchet, M.D. de Smet, M.J.F. Farall, *Polymer*, **20**, 675-680 (1979)
5-A. Revillon, A. Guyot, Q. Yuan, P. da Prato, *Reactive Polymers*, **10**, 11-25 (1989)

6- R.H. Yocum in *Functional Monomers*, p.518, Dekker 1973
7-W. Huang, B. He, *Chinese J.Reactive Pol.*, **1**, 61-70 (1992)

Keywords
Acid catalysis, Bisphenol A preparation, polymer supported catalysts, bifunctional catalysts, reactive polymers