Synthesis and Study of a Polymer for the Analysis and Removal of Phenols from Aqueous Solutions

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SYNTHESIS AND STUDY OF A POLYMER FOR THE ANALYSIS AND REMOVAL OF PHENOLS FROM AQUEOUS SOLUTIONS†

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ABSTRACT

By copolymerization of 4-benzylidene aminophenyl methacrylate with β-hydroxyethyl methacrylate and the crosslinker ethylene dimethacrylate (also in the presence of petroleum ether or different alcohols), normal and macroporous polymeric samples were synthesized. After cleaving off the protective group and diazotization, these polymeric samples can bind phenols through azo coupling. By applying ester hydrolysis, the azo dye formed on the polymer can be split off and determined quantitatively. The stability of the polymeric samples in their diazotized form was investigated, including some methods of stabilization. The effect of several heavy metal ions on the long-time stability of the diazotized polymer is described. By choosing suitable solvents for the synthesis of macroporous polymeric samples in the polymerization, the mechanical stability was optimized.

INTRODUCTION

Even small traces of phenol badly affect the taste and the smell of drinking water, and in higher concentrations they actually show toxic effects. Therefore their removal and also the possibility of quantitative analyses play an important role in

†Dedicated to Professor Otto Vogl on the occasion of his 65th birthday.

water technology processes such as drinking water, sewage treatment, and water for industrial uses.

Analytical methods used up to now are paper chromatography, gas chromatography, and/or high-performance liquid chromatography [1–6] as well as colorimetric methods [7, 8]. The sensitivity of these methods is usually very low. The removal, enrichment, and subsequent colorimetric determination have been extremely problematic.

However, a solution for this problem is offered in the form of a synthesized resin which contains diazonium groups and is therefore able to bind phenol-forming azo dyes via azo coupling. Furthermore, the dye, which is bound to the resin via ester groups, can be cleaved from the polymer by the aid of hydrolysis and then determined quantitatively by colorimetry.

Because of the comparatively poor stability of diazonium ions, it is necessary to investigate methods of stabilizing aromatic diazonium compounds and to synthesize a polymer containing diazonium groups which can be stored, if necessary, at lower temperatures.

STUDIES ON THE STABILIZATION OF
AROMATIC DIAZONIUM COMPOUNDS

It is known from the literature [9–11] that the stabilization of diazonium salts can be achieved by lowering the temperature, by introducing appropriate substituents into the aromatic system, and by adding acids and certain counterions.

At simultaneously varying temperatures, the stabilizing and/or destabilizing effects of several substituents such as hydroxy, carboxyl, acyloxy, methyl, and methoxy groups were studied [10] (see Table 1). These effects can be explained by the mesomeric limiting formulas of the phenyldiazonium cations:
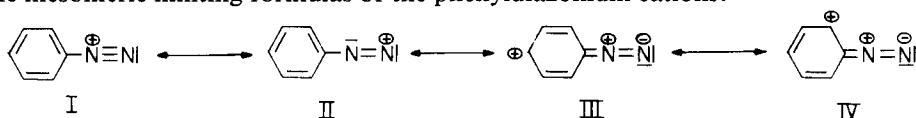
In Structure I, the electronic configuration of the nitrogen atoms is similar to that of molecular nitrogen, indicating decomposition occurs via this leaving group. Electron-withdrawing substituents (e.g., $-$COOH) favor Structures III and IV stabilizing the diazonium ion. This effect decreases with increasing distance of the electron-withdrawing substituents of the diazonium group [10].

For groups possessing an electron-donating character, the interpretation is more complex. Hydroxy groups, for instance, have a negative inductive effect ($-$I-effect) but a strong donating effect through resonance ($+$M-effect). According to Allinger [15], the $-$I-effect of the sp^3-hybridized O atom is not as large as its $+$M-effect, which can be described by the following mesomeric formula for hydroxyphenyl diazonium cations:
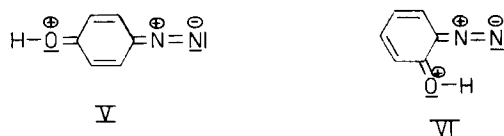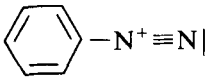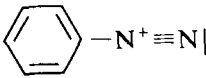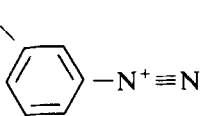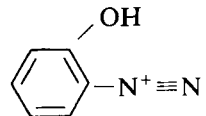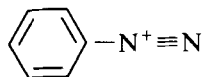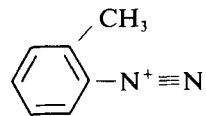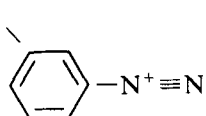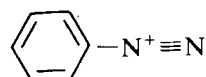
TABLE 1. Half-Lifetimes of Some Aromatic Diazonium Cations at 20–25°C and at 5°C

Diazonium cation	Half-lifetime	
	At 20–25°C (in days)	At 5°C (in days)
$\bigcirc\!\!-N^+\!\equiv\!N\vert$	0.3	3.7
$HO\!-\!\bigcirc\!\!-N^+\!\equiv\!N\vert$	100	—[b]
$HO\!-\!\bigcirc\!\!-N^+\!\equiv\!N\vert$ (HO ortho)	0.01[a]	0.5[a]
$\bigcirc\!\!-N^+\!\equiv\!N\vert$ (OH meta)	20[a]	—
$HOOC\!-\!\bigcirc\!\!-N^+\!\equiv\!N\vert$	1.25	18
$\bigcirc\!\!-N^+\!\equiv\!N\vert$ (CH_3 ortho)	0.04[a]	1[a]
$H_3C\!-\!\bigcirc\!\!-N^+\!\equiv\!N\vert$ (H_3C meta)	0.05[a]	1.1[a]
$H_3C\!-\!\bigcirc\!\!-N^+\!\equiv\!N\vert$	2.0[a]	70[a]

(continued)

TABLE 1   (continued)

Diazonium cation	Half-lifetime	
	At 20–25°C (in days)	At 5°C (in days)
$HOOC-H_2C-\text{⟨C₆H₄⟩}-N^+\equiv N\|$	0.6	—[b]
$H^3C-CO-\text{⟨C₆H₃(HO)⟩}-N^+\equiv N\|$[c]	4	—[b]
$H_3C-CO-O-\text{⟨C₆H₄⟩}-N^+\equiv N\|$[d]	0.5	—[b]
$H_2C=\overset{CH_3}{\underset{}{C}}-CO-O-\text{⟨C₆H₄⟩}-N^+\equiv N\|$[e]	1.5	—[b]

[a]Values taken from Ref. 10.
[b]Measured at room temperature only.
[c]Synthesis according to Ref. 12.
[d]Synthesis according to Ref. 13.
[e]Synthesis according to Ref. 14.

These two formulas correspond with Structures III and IV, explaining the stabilization. The hydroxy group in the *m*-position cannot produce the mesomeric effect, and therefore destabilization occurs.

Methyl groups with their + I-effect also act in the same way: in the *p*-position, Structure IV is preferred; in the *m*-position, destabilization results; in the *o*-position, destabilization occurs, which Ullmann [10] traces back to steric hindrance. In the 3-hydroxy-4-methoxybenzene diazonium cation, the methoxy group with its + M-effect also acts as a stabilizer (see also Table 1). Furthermore, the *p*-carboxybenzene diazonium cation is also more stable relative to the unsubstituted benzene diazonium cation because of the electron-withdrawing effect of this substituent. Such a stabilization was also found for *p*-acyloxybenzene diazonium cations [10] (see Table 1).

Summarizing, electron-withdrawing substituents always stabilize aromatic diazonium cations, but electron-donating substituents only stabilize in the *o*- or *p*-positions, whereas in the *m*-position they destabilize.

The stabilization of diazonium cations by acids is not described in this paper because, according to Ullmann [10], only very high concentrations of acids give an appreciable effect. However, because the reactive diazonium group was to be connected to the polymer by an ester linkage, this method of stabilization was excluded due to the danger of hydrolysis.

According to the literature [9–11], diazonium cations can also be stabilized by formation of a donor-acceptor complex with naphthalene derivatives, especially those containing sulfonic acids. Furthermore, it is also known [8] that diazonium cations can be stabilized by certain anions such as BF_4^- and FSO_3^- in the solid state.

All these arguments allow for the structural design of an appropriate polymer, which is based on the following monomer:

$$H_2C=\overset{\overset{\displaystyle CH_3}{|}}{C}-CO-O-\!\!\left\langle\!\!\!\bigcirc\!\!\!\right\rangle\!\!-NH_2$$
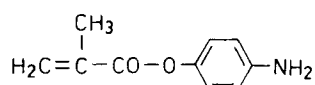
SYNTHESIS OF A POLYMER WITH DIAZONIUM GROUPS

4-Aminophenyl methacrylate can be prepared according to the method of Ringsdorf and Greber [14], where the amino group of *p*-aminophenol was protected by a benzylidene group.

$$HO-\!\!\left\langle\!\!\!\bigcirc\!\!\!\right\rangle\!\!-NH_2 + OHC-\!\!\left\langle\!\!\!\bigcirc\!\!\!\right\rangle \xrightarrow[-H_2O]{} HO-\!\!\left\langle\!\!\!\bigcirc\!\!\!\right\rangle\!\!-N=CH-\!\!\left\langle\!\!\!\bigcirc\!\!\!\right\rangle$$

$$\xrightarrow[-KCl,\ -H_2O]{+CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-CO-Cl\ /\ KOH} CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-CO-O-\!\!\left\langle\!\!\!\bigcirc\!\!\!\right\rangle\!\!-N=CH-\!\!\left\langle\!\!\!\bigcirc\!\!\!\right\rangle$$

<u>1</u>
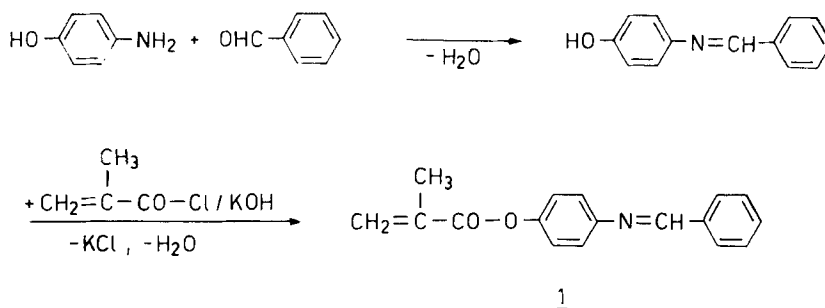
The cleaving off of the protective group in slightly acid medium does not necessarily have to be carried out on the monomer, because it is later removed automatically during diazotization of the polymer. Therefore, 4-benzylidene aminophenyl methacrylate (<u>1</u>) was used for the polymerization.

In order to obtain a strongly crosslinked, macroporous, and therefore quickly reactive polymer, petroleum ether and several alcohols (see Table 2) have been found to be useful for the preparation of macroporous polymers.

2-Hydroxyethyl methacrylate (HEMA, <u>2</u>) was chosen as a comonomer for achieving good hydrophilicity and swelling ability of the polymeric samples.

$$CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-CO-O-CH_2-CH_2-OH$$

<u>2</u>
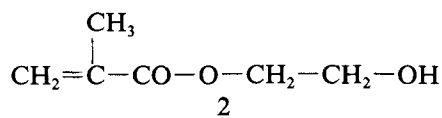
TABLE 2.   Relation of the Sieving Fractions of Polymer $\underline{4}$
Depending from the Solvent Used for the Polymerization

	Sieving fraction, %		
Solvent	<0.1 mm	0.1–0.2 mm	0.2–0.5 mm
Ethanol	29	12	59
Isopropanol	28	14	58
Propanol	23	13	64
2-Butanol	11	22	67
Cyclohexanol	7	21	72
Petroleum ether, 80–90°C	65	23	12

Divinylbenzene (DVB) has been found to be an unsuitable crosslinker because about one-third of the resulting polymer was still extractable by acetone, and the remaining polymer presented a much higher amount of HEMA in the IR spectra than the soluble part. Thus, the true compositions of the polymeric samples are unknown. Such problems did not arise with ethylene dimethacrylate ($\underline{3}$).

$$CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-CO-O-CH_2-CH_2-O-CO-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2$$
$$\underline{3}$$
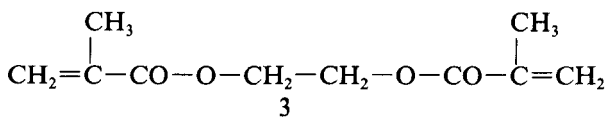
In this case, the monomers were transferred quantitatively into insoluble polymeric networks.

A similar polymer for the immobilization of enzymes was prepared by Manecke and Polakowski [16]. They synthesized a polymer analogous to Polymer $\underline{4}$ (see below), containing a nitro group instead of the benzylideneamino group, which was subsequently transformed into an amino group by reduction. After diazotization, this polymer was coupled with enzymes [16].

Polymerization was carried out with 40 mol% $\underline{1}$, 40 mol% $\underline{2}$, and 20 mol% $\underline{3}$ for 24 hours at 80°C in a bomb. Azobisisobutyronitrile (AIBN) (1 wt%) was added as an initiator for radical polymerization. The yield of insoluble Polymer $\underline{4}$ was practically quantitative. The components were soluble in hot acetone to less than 1%.

$$\underline{4}$$
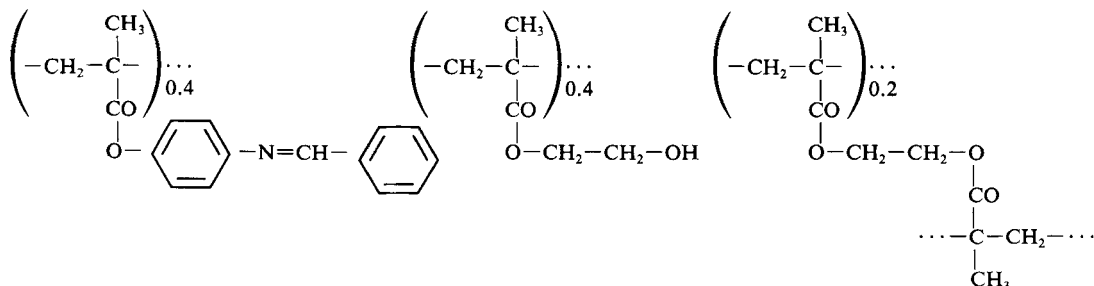
For conditioning, the screening fraction <0.1 mm is separated from the 0.1–0.2 and 0.2–0.5 mm fractions. The coarser fractions are suitable as filling materials for columns with good mechanical stability of the polymer. The mechanical stability is relatively low when petroleum ether is used as a solvent for the polymerization, so other solvents were also studied, as can be seen in the results shown in Table 2.

Cyclohexanol, which produces the best results, has the disadvantage of being difficult to remove completely from the polymer because of its high boiling point. In the series of alcohols, an increase of the mechanical stability of the polymer with increasing chain length is generally observed. Petroleum ether with a boiling range of 80–90°C gives the worst result because at 80°C the monomer needs about 5 times the amount of petroleum ether dissolution. This results in a network with low mechanical stability. With alcohols, only about double the amount of solvent in relation to the monomers is required to obtain a good solution at 80°C, which explains the higher mechanical stability compared with polymeric samples produced with petroleum ether. The best results were found with ethanol as solvent.

Elemental analysis of the polymer, freed from the protective group by treatment with hydrochloric acid, confirms the structure of the polymer (see the Experimental Section).

Scheme 1 describes the preparation of the polymer, cleavage of the protective group, diazotization, coupling with phenol, and cleavage of the dye.

After polymerization, the protective group was cleaved by hydrochloric acid treatment and then diazotization was carried out in one step. The polymer was stirred with 0.1 N HCl, and then a $NaNO_2$ solution was added.

The IR spectra of the polymer without protective groups shows an absorption band for the OH group (from $\underline{2}$) at 3200–3600 cm^{-1}. From $\underline{1}$, the band is superimposed by two more bands at 3380 and 3460 cm^{-1}, corresponding to the NH$_2$ vibration. Out-of-plane deformation of the NH$_2$ appears at 1630 cm^{-1}, the stretching vibration of the aromatic CH appears at 3060 cm^{-1}, and the vibration for the aromatic ring appears at 1510 and 1580 cm^{-1}. Moreover, a characteristic band at 830 cm^{-1} appears for the 1,4-disubstituted aromatic system.

In the diazotized form of the polymer, the IR spectrum changes as follows: the three NH$_2$ bands disappear; a sharp peak at 2275 cm^{-1} appears for the $-N^+\equiv N|$ group.

EXPERIMENTAL

Polymer $\underline{4}$ was characterized by means of IR spectra (Perkin-Elmer 580 B, KBr pellets). Electron spectra of the dyestuff in H_2O and stability measurements were carried out (and/or plotted) with a Beckman DK-2A spectrometer.

Investigation of Stability of Low Molecular Weight Diazonium Compounds

The diazonium compounds of the following amines were investigated: aniline, p-aminophenol, p-aminobenzoic acid, p-aminophenylacetic acid, 3-hydroxy-4-methoxy aniline, 4-aminophenylacetate, and 4-aminophenylmethacrylate (see Table 1).
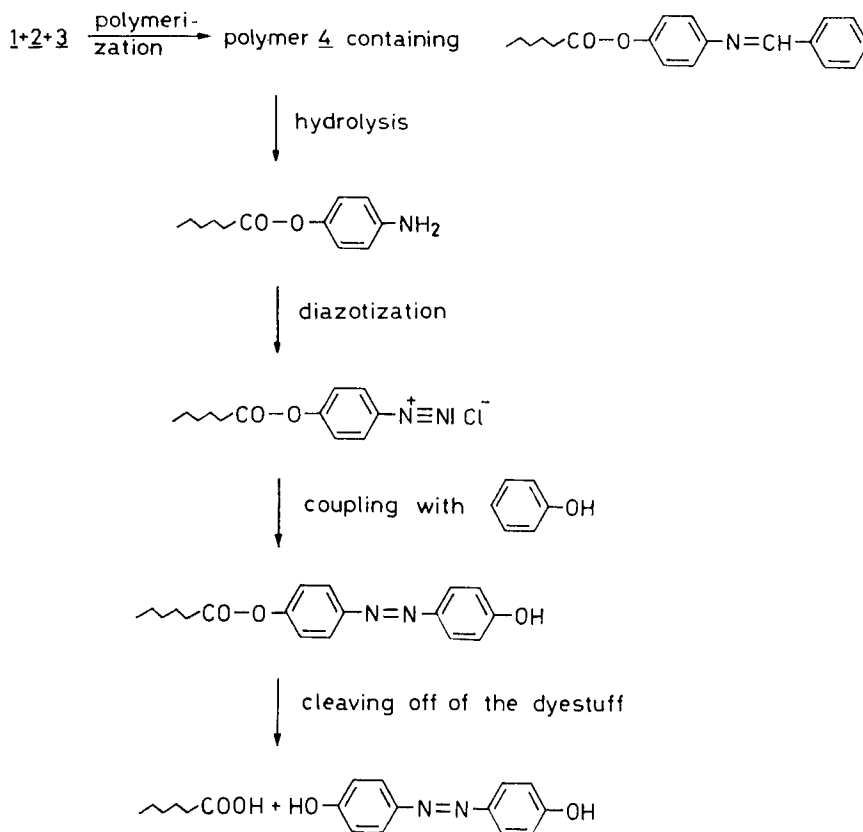
SCHEME 1.

Diazotization was carried out by reaction of 10 mmol of the amine to be investigated in 10 mL half-concentrated HCl with 10 mmol $NaNO_2$ as a 2.5-M aqueous solution. The diazonium salt solution was then diluted to such an extent that on coupling with phenol, the dyestuff concentration was well suited for spectroscopic investigation.

For Aniline

Aniline [0.93 g (10 mmol)] was stirred with 10 mL half-concentrated HCl while being cooled with an ice/NaCl mixture. $NaNO_2$ [0.69 g (10 mmol)] in 4 mL H_2O was added dropwise so that the temperature in the reaction vessel did not rise above 5°C. After addition, the mixture was stirred for another 10 minutes and the excess HNO_2 removed with urea. The solution was diluted to a concentration of 5 $\times$ 10^{-4} M. For coupling with phenol, 5 mL of the diazonium chloride solution was added to 5 mL 2 $\times$ 10^{-3} M phenol solution and then buffered with 1 mL buffer solution to give pH 9. [The buffer was prepared from 5.3 g (0.1 mol) NH_4Cl and 5.5 g (0.1 mol) 35% NH_4OH and diluted to 50 mL.] The resulting dyestuff was measured in comparison to H_2O as the reference solution.

Coupling with phenol was carried out after definite time periods (from several hours up to 400 days) after the diazotization and resulted in a decrease of dye formation due to the decreasing concentration of diazonium cations. The half-life time of the diazonium salt was determined from the resulting curves.

Dependence of Stability on Temperature

The suitably diluted diazonium salt solution was split up and the solutions kept at room temperature (20–25°C) and/or in the refrigerator (5°C) and studied over a period of several months. The results are summarized in Table 1.

Stabilization by the Addition of Salts

One hundred millimoles aniline, p-aminophenol, and p-aminobenzoic acid were each diazotized as described above, diluted to 100 mL (i.e., the resulting diazonium salt solutions became 1 M) and 1 mL of this solution was added to 1 L of 0.1, 0.5, 1, and 2.5 M $NaBF_4$ solutions by using a pipette. These solutions were then 10^{-3} M with regard to diazonium cations. They were kept at 5°C and coupled with phenol after certain time periods as described above, and the results are shown in Table 3.

The tests with NaCl and $NaFSO_3$ were carried out analogously.

Synthesis of Copoly[4-benzylidene Aminophenyl Methacrylate-(40)-2-hydroxyethyl Methacrylate-(40)-ethylene Dimethacrylate-(20)] (4)

4-Benzylidene aminophenyl methacrylate (1) [1.60 g (6 mmol)], 0.80 g (6 mmol) 2-hydroxyethyl methacrylate (HEMA, 2) and 0.60 g (3 mmol) ethylene dimethacrylate (3) were placed in a 30-mL bomb. Azobisisobutyronitrile [30 mg (1 wt%)] was added. The mixture was frozen in liquid N_2 and evacuated to remove O_2. Then it was thawed to remove O_2 which was dissolved in the liquid and gassed with N_2. This procedure was repeated twice, and finally the mixture was frozen and evacuated. The bomb was unfrozen and kept for 1 day at 80°C. The resulting translucent, glasslike, brittle, beige-colored solid was then dried at 80°C *in vacuo*.

Polymer 4 was treated with boiling acetone; the acetone phase evaporated to dryness, leaving approximately 30 mg (1%) of soluble components. To expel the acetone, the residue was treated with ether and then dried. Yield: 2.95 g = 98.5% of the theoretical value.

TABLE 3. Half-Life Time of 5×10^{-4} Benzenediazonium Tetrafluoroborate at 5°C in Various Concentrated $NaBF_4$ Solutions

$NaBF_4$ concentration, M	Half-life time, h
0	90
0.1	90–100
0.5	90–100
1.0	700–750

For elemental analysis, the protective group was split off by means of hydrochloric acid (1 N, 60 minutes). One gram of Polymer $\underline{4}$ yielded 0.83 g (quantitative). $[(C_{10}H_{11}NO_2)_{0.4}(C_6H_{10}O_3)_{0.4}(C_{10}H_{14}O_4)_{0.2}]_n \cdot (162.4)_n$. Found: C, 61.86; H, 7.11; N, 3.28%. Calculated: C, 62.07; H, 6.90; N, 3.45%.

The application of solvents resulted in macroporous polymeric samples having a claylike appearance (see below).

Diazotization of Polymer $\underline{4}$

To cleave off the benzylidene protecting group, 2.00 g of Polymer $\underline{4}$ was stirred for 30 minutes in 100 mL 0.1 N HCl. To diazotize, a solution of 1.00 g $NaNO_2$ together with a small amount of water was added dropwise to this suspension of the polymeric 4-aminophenyl ester at a temperature well below 5°C. After addition, the mixture was stirred for another 30 minutes, the excess HNO_2 was destroyed by urea, suctioned off, and the mixture washed several times with acetone and subsequently with ether in order to remove the water, the ether being removed *in vacuo*.

Preparation and Cleaving off the Azo Dyestuff at the Polymer

Diazotized polymer (50 mg) was stirred for 30 minutes with 30 mL (30 mmol) of 10^{-2} N phenol solution and 5 mL buffer solution (see above). The polymer turned to an orange color. To cleave off the dyestuff, the polymer (after vacuum filtration) was boiled for 1 hour with 50 mL of 5 N NaOH under reflux. The solution turned to a dark red color. After vacuum filtration it was brought to pH 13 and then measured colorimetrically.

Preparation of Macroporous Granular Fractions of Polymer 4

The polymerization was carried out as described above while varying the solvent. Either 5 mL Ethanol, isopropanol, propanol, 2-butanol, or cyclohexanol or 25 mL petroleum ether (boiling range 80–90°C, 100 mL bomb tube) were added as a solvent for the monomer. After 1 day of polymerization at 80°C using cyclohexanol and drying *in vacuo*, a brittle, glasslike, yellowish, transparent product was received. With all other solvents, the polymeric samples had a claylike appearance.

The easily wettable polymers (except when using petroleum ether) were carefully crushed, kept 1 hour in H_2O so they could swell, and were then passed through screens with mesh measurements of 0.5, 0.2, and 0.1 mm. The fractions were sucked off, dried *in vacuo*, and weighed. The size distribution is shown in Table 2.

Stability of the Dyestuff

A 5×10^{-5} M solution of 4,4'-dihydroxyazobenzene (prepared as described in Ref. 15) was measured colorimetrically in 5 N NaOH and in 5 N HCl. The absorption maxima were 455 nm in the alkaline range and 490 nm in the acid range. The solutions were kept for 3 days at room temperature and then measured once more (the spectra did not change); then the solutions were boiled under reflux. The alkaline solution remained unchanged after 1 day whereas the maximum at 490 nm in the acid solution decreased and two new peaks at 340 and 300 nm appeared. After boiling the acid solution for 1 day, the maximum at 490 nm disappeared completely.

Determination of the Coupling Time of Polymer 4

Diazotized Polymer 4 (50 mg) was stirred with 30 mL of 10^{-2} N phenol solution until the polymer was completely saturated. After the addition of 5 mL NH_3/NH_4^+ buffer (see above), the coupling was interrupted after periods of 1, 5, 30, and 60 minutes. The dye was separated from the polymer after vacuum filtration by boiling for 1 hour with 50 mL of 5 N NaOH. After suitable dilution, the dyestuff was measured colorimetrically at pH 13.

Cleaving Time of the Azo Dyestuff

Diazotized Polymer 4 (500 mg) was stirred with 250 mL of 10^{-2} N phenol solution and 50 mL NH_3/NH_4^+ buffer (see above), filtered, and dried *in vacuo*. Samples of 50 mg were then treated for certain time periods (see above) with 50 mL of 5 N NaOH either under cooling and/or at the boiling temperature. After suction and dilution, the solution was measured colorimetrically at pH 13.

Activity of the Polymer

A calibration curve was obtained by preparing solutions of 4,4'-dihydroxyazobenzene in 0.1 N NaOH in the concentration range of 1×10^{-5} to 8×10^{-5} M, measuring colorimetrically, and plotting the extinction against the concentration. Thereafter, 50 mg of Polymer 4 (anion: BF_4^-; $\rightarrow 9.8 \times 10^5$ mol diazonium cations per 50 mg) was coupled with phenol as described above and the dyestuff was separated from the polymer with 50 mL of 5 N NaOH. The solution was diluted to 1 L, brought to pH 13, and measured colorimetrically. The concentration of the actual coupling diazonium cations was determined by comparing it with the calibration curve.

H₂O Uptake of Polymer 4

To determine the uptake capacity of Polymer 4 for water, 1.00 g samples of the polymer in diazotized and undiazotized forms were kept in a desiccator with 100% humidity and weighed after certain time periods.

Investigations of the Stability of Polymer 4

Under Solution

Under H₂O. Samples of diazotized Polymer 4 (50 mg) were kept under 10 mL of demineralized H_2O at 5°C and at room temperature. After certain time periods the reactions described above (coupling with phenol, splitting off of the azo dyestuff) and the colorimetrical measurement at pH 13 were carried out. The measured values of extinction at $\lambda_{max} = 455$ nm were plotted against the storage time, and the half-life time was determined from the curve (see Table 4).

Under NaCl Solution. As above, 50 mg samples of diazotized Polymer 4 were each treated with 10 mL H_2O and thereafter 3.6 g (or 1.8 g) NaCl was added to achieve a concentrated (or a half-concentrated) solution. The reaction and the determination of the half-life time were the same as above.

TABLE 4. The Stability of the Diazotized Polymer $\underline{4}$ and Its Dependency on Temperature, Counterions, Complex Functions, and Heavy Metal Ions

	Temperature			
	5°C (in days)	20–25°C (in days)	35°C (in days)	50°C (in days)
1. Under solution:				
a) As Cl⁻ under H_2O	400^a	8–12 30–35		
b) Under half concentrated NaCl solution	—	8–12		
c) Under half concentrated $NaBF_4$ solution	—	8–10		
d) Under concentrated $NaFSO_3$ solution	—	4–5		
e) Complex formation with disodium naphthalene-1,5-disulfonate:				
1 equivalent	$\infty^{a,b}$	$110–120^a$		
4–20 equivalents	$\infty^{a,b}$	$120–140^a$		
10 equivalents	∞^b	25–35		
f) Disulfonate/BF_4^-	∞^b	20–25		
2. As dry material:				
a) As Cl⁻	$300–350^a$	$35–45^a$	$12–14^a$	2^a
b) As FSO_3^-	$450–600^a$	$80–100^a$	$16–18^a$	—
c) As BF_4^-	∞^b	$350–450^a$	$44–55^a$	$6–8^a$
d) With napthalene-1,5-disulfonate	∞^b	$300–350^a$	$30–40^a$	$2.5–3.5^a$
e) With BF_4^-/disulfonate	∞^b	$300–400^a$	—	—
3. By addition of heavy metals under solution:				
a) Fe^{2+} (56 ppm)		$15–20^a$		
b) Cu^{2+} (48 ppm)		$10–15^a$		
c) Cu^+ (4 ppm)		$10–15^a$		
d) Pb^{2+} (52 ppm)		$30–35^a$		

[a]Values measured on the "purified polymer."
[b]Decrease of activity not measurable within a period of more than 1 year.

Under NaBF₄ Solution. To achieve a half-concentrated solution, 4.5 g $NaBF_4$ was added to every sample.

Under NaFSO₃ Solution. Samples (50 mg) were treated directly with 10 mL of concentrated $NaFSO_3$ solution (0.5 g/10 mL). Due to the low salt concentration, the wettability was not hindered.

Under Disodium Naphthalene-1,5-disulfonate Solution.   A series of 50 mg samples (1 × 10^{-4} mol diazonium cations) were prepared and brought to reaction by the addition of 17 mg (1 equiv), 66 mg (4 equiv), 166 mg (10 equiv), or 332 mg (20 equiv) of disodium naphthalene-1,5-disulfonate in 10 mL H_2O.

Under NaBF₄ and Disodium Naphthalene-1,5-disulfonate Solution.   Samples (50 mg, 1 × 10^{-4} mol diazonium cations) were each treated with 166 mg (10 equiv) disodium naphthalene-1,5-disulfonate and dissolved. $NaBF_4$ (4.5 g) was then added and dissolved in order to achieve a half-concentrated solution. This is precisely the amount of $NaBF_4$ which does not cause precipitation of the disulfonate.

As a Dry Material

In the Cl^- Form.   Because of its higher stability, the diazotized Polymer 4 in the Cl^- form was investigated at 5°C, room temperature, 35°C, and 50°C. At certain times, 50 mg samples were taken, treated with 50 mL of 5 N NaOH, and measured as described above.

In the FSO_3^- Form.   Diazotized Polymer 4 (5.00 g) in the Cl^- form was stirred for 30 min with 500 mL concentrated $NaFSO_3$ solution, suctioned, washed with acetone and then ether, dried *in vacuo*, divided, kept, as above, at 5°C, room temperature, and 35°C, and analyzed.

In the BF_4^- Form.   As above, but stirred with concentrated $NaBF_4$ solution.

As a Complex with Disodium Naphthalene-1,5-disulfonate

Treatment as above, but with 10% disodium naphthalene-1,5-disulfonate solution.

Combination of Complex and Salt Stabilization

As above, but the diazotized Polymer 4 was stirred with a solution which contained 10% $NaBF_4$ and 10% disodium naphthalene-1,5-disulfonate.

The Influence of Heavy Metal Ions

With Fe^{2+}. $FeSO_4 \cdot 7H_2O$ (1.39 g) (MW = 278) was dissolved in 100 mL H_2O (2.8 g Fe^{2+}/L). This solution was diluted 50 times, so that the concentration was 56 ppm Fe^{2+}. Samples of 50 mg of the diazotized Polymer 4 were kept under 10 mL of this solution, treated with 50 mL of 5 N NaOH, and analyzed as above.

With Cu^{2+}. $CuSO_4 \cdot 5H_2O$ (1.25 g) (MW = 250) was dissolved in 100 mL H_2O (3.2 g Cu^{2+}/L). One and a half milliliters of the solution was diluted to 100 mL (48 ppm Cu^{2+}). Further treatment as above.

With Cu^+.   A concentrated CuCl solution (62 mg/L) was diluted 1:10 (4 ppm Cu^+). Further treatment as above.

With Pb^{2+}. $Pb(NO_3)_2$ (1.65 g) (MW = 331) was dissolved in 100 mL H_2O. This solution was diluted 200 times (52 ppm Pb^{2+}). Further treatment as above.

RESULTS AND DISCUSSION

General Studies of the Polymer

The stability of the azo dye 4,4'-dihydroxyazobenzene was studied in acid and alkaline media. In acid medium the dye was completely destroyed after boiling for 1 day in 5 N HCl. On the other hand, it proved to be absolutely stable in 5 N NaOH. Furthermore, cleavage of the azo dye from the polymer (ester hydrolysis) in acid medium is not quantitative as in alkaline medium, so cleavage in aqueous NaOH is recommended.

Investigations were carried out to determine the coupling time of phenol to the polymer. In a slightly basic region (NH_3/NH_4Cl buffer), a surplus of phenol was added to the diazotized polymer and the reaction was interrupted after a certain time. The polymer was then refluxed with 5 N NaOH, and the extinction of the resulting dyestuff solution was measured after adequate dilution at pH 13 and λ_{max} = 455 nm. After only 1 minute, 85% of the possible maximum that had been found after about 5 minutes coupling time was reached.

For cleavage of the dye from the polymer, the resin coupled with phenol was treated differently for various times with boiling 5 N NaOH at room temperature. It was found that the hydrolysis at room temperature was incomplete, while after 15 minutes of refluxing with NaOH the dye had been cleaved quantitatively.

The activity of the polymer was also determined, i.e., the number of coupled diazonium ions in comparison to the amount of monomer employed. A calibration curve of the resulting dye, 4,4'-dihydroxyazobenzene [17], at pH 13 and λ_{max} = 455 nm was plotted, and the extinction of the dyestuff, which resulted after coupling with an excess of phenol and cleavage from the polymer, was compared with the calibration curve. About 75–80 mol% of the amino compound employed was found to be reactive.

The residual concentration of phenol within the aqueous phase after coupling to the diazotized polymer was also determined. Phenol concentrations $< 10^{-4}$ mol phenol/L could not be detected quantitatively by gas chromatography.

We also investigated the water absorption capacity of undiazotized and diazotized polymers at 100% atmospheric humidity. The undiazotized polymer was saturated with water after 3–5 days and had absorbed 7.5–9% by weight. The diazotized polymer proved to be very hygroscopic. It reached its full saturation point after 8 months with a water absorption of 330% by weight.

Stability Studies

Stability studies were first carried out on low-molecular weight compounds with tetrafluoroborates and fluorosulfates to examine the possibility of repressing the dissociation equilibrium by high concentrations of such salts to the end that stabilization would become noticeable. For benzene diazonium tetrafluoroborate in $NaBF_4$ solutions of varying concentrations (see Table 3), a strong stabilization effects was seen, but similar effects were not observed either with p-hydroxybenzene diazonium tetrafluoroborate or with p-carboxybenzene diazonium tetrafluoroborate. Other salts, such as NaCl and $NaFSO_3$, also showed no effect.

The stability of the diazotized polymer was carried out at various temperatures with the addition of various salts and the formation of complexes. Some measurements were also carried out in the presence of heavy metal ions (see Table 4).

The diazotized polymer was first studied in the Cl$^-$ form in swollen form in demineralized water of concentrated or half-concentrated NaCl, NaBF$_4$, and NaFSO$_3$ solutions. The poor wettability of the polymer became a problem with highly concentrated salt solutions. The polymer was therefore soaked with water first and then the required concentration was realized by the addition of salt.

As can be seen from Table 4, Samples 1a–d contain added salts (in comparison with the saltless solution), but this did not improve stability.

The data for the chloride were found by repeated measurements on newly prepared polymeric samples. The only difference between the preparation of the first polymeric samples and the new ones was that the benzaldehyde for the protection of the NH$_2$ group was purified by repeated distillation before use (leading to the "purified polymer").

It was therefore suspected that the first polymer, prepared with technical benzaldehyde, carried heavy metal ions which caused a catalytic decomposition of the diazonium cations. Corresponding measurements of polymeric samples in their diazotized form as chlorides with added heavy metal salts are summarized in Table 4, Samples 3a–d.

The presence of Fe^{2+}, Cu^{2+}, and Cu$^+$ ions caused considerable destabilization, whereas the presence of Pb^{2+} ions had no influence on the stability of the polymeric samples. The less soluble Cu$^+$ exhibit the same destabilization at a lower concentration than the other heavy metal ions. The electronic spectra of the resulting dyestuff samples showed side products formed by decomposition of the diazonium ion in the presence of Cu$^+$ ions. These observations coincide with the well-known Sandmeyer reaction, which takes advantage of this instability of the diazonium ion in the presence of Cu$^+$ ions.

Because the addition of salts to the solution evidently did not improve stabilization, measurements with polymeric samples purified of heavy metals were not repeated (see Table 4, Samples 1b–d).

Investigations were performed on polymeric samples in solution to which various amounts of disodium naphthalene-1,5-disulfonate (donor-acceptor complex formation) had been added. For the "purified polymer" it was possible to establish the addition of even 1 equivalent of disulfonate resulted in strong stabilization (by a factor of 3–4) which could only be slightly improved by the addition of higher amounts of disulfate (4–20 equivalents) (see Table 4, Sample 1e).

At 5°C the samples studied were already so stable that no relevant decrease of activity could be observed within a reasonable time. On the basis of Table 5, it can be established that even low concentrations of disulfonate (e.g., 1 equivalent) are responsible for a strong increase in stability, which reaches its maximum at about 10 equivalents.

Combinations in solution, e.g., disodium naphthalene-1,5-disulfonate with NaBF$_4$, were also tested, but we could only observe a decrease of the complex stabilization by BF$_4^-$ ions (see Table 4, Sample 1f, values for 20–25°C).

The stability of polymeric samples in their diazotized form was also studied in the solid, unswollen state. The results are summarized in Table 4, Samples 2a–e.

The diazotized polymeric samples in the fluorosulfonate form (see Table 4, Sample 2b), which were prepared by stirring the chloride form with saturated NaFSO$_3$ solution and subsequently filtering and drying, proved to be 2 times more stable at room temperature and at 5°C than the chloride form. The values approximated one another at higher temperatures.

TABLE 5.   Stabilization of Diazotated Polymer
4 in Disodium Naphthalene-1,5-disulfonate Solu-
tion at Room Temperature

Number of added equivalents	Half-lifetime, days
0	30– 35
1	110–120
4	130–140
10	150–160
20	150–170

Polymeric samples in the tetrafluoroborate form (see Table 4, Sample 2c) were prepared in the same way as mentioned above. They reached a stability which was 10 times higher than the chloride form at room temperature. At 5°C the samples were so stable (as with Samples 1e and 1f) that a slight reduction in activity could be detected only with measurements carried out after more than 1 year.

Similar results were reached when stabilization was realized by complex formation with disodium naphthalene-1,5-disulfonate (Table 4, Sample 2d).

During the interchange of the counterion, the diazotized polymer was prepared as above. It was stirred with a solution of sodium naphthalene-1,5-disulfonate in water and dried after filtration. When disulfonate was combined with $NaBF_4$, no synergistic effect was observed (see Table 4).

OUTLOOK AND FURTHER APPLICATION

This reactive polymer with its long stabilization time can be stored (especially at refrigerator temperatures) with little or no loss of activity. This allows it to be used in typical analytical laboratories which do not have the possibility of synthesizing a reagent for phenols.

It is not only useful for the detection of phenols, but due to its reactive diazonium groups it can be used as a carrier polymer for the immobilization of amino acids and proteins. It is especially useful for the immobilization of enzymes and other materials of biological interest which can be coupled with diazonium salts [16]. Because of their stability, these materials should be of great utility in the biochemical and medical fields but not necessarily of interest in the field of synthetic chemistry.

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