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PREPARATION AND PROPERTIES OF NOVEL CATIONICALLY ACTIVE OLIGO-*p*-METHOXYSTYRYL- SILICA COMPOSITES

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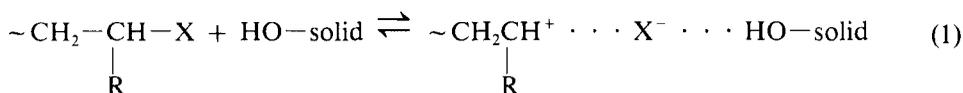
ABSTRACT

The preparation of cationically active oligo-*p*-methoxystyrene-silica composites by cationic interfacial polymerization is described. In addition to the effective preparation of the interfacial initiator, *p*-methoxybenzylum-hydrogen sulfate-silica, and *p*-methoxybenzylum-trifluoroacetate-silica, a procedure to yield new kinds of composites is reported. The outstanding properties of the “living” oligo-*p*-methoxystyryl-hydrogen sulfate-silica is demonstrated by means of zeta potential measurements, solid-state ¹³C-NMR spectroscopy, UV/Vis spectroscopy, and electron scanning microscopy.

INTRODUCTION

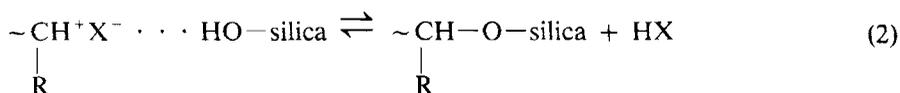
We recently reported on the cationic interfacial polymerization of *p*-methoxystyrene by means of triphenylmethylum-halide-aerosil initiation in 1,2-dichloroethane [1]. The interfacial polymerization undergoes conversion into two products, extractable polymers with narrow MWDs and polymer and oligomer-silica composites which bear Si—O—C bonds and cationically active polymer chains which depend on the counterion and the nature of the growing cation [2]. The principle of cationic interfacial polymerization [1] is based on the fact that the coordination of the active chain carrier at acceptor surface groups occurs via the corresponding

counterion, as demonstrated in Eq. (1). Other principles of polymer grafting reactions onto solid surfaces were reviewed by Laible and Hamann [3].



Counterions which approach interfacial ion-pair propagation in Eq. (1) include fluoride, chloride, bromide, hydrogen sulfate, trifluoroacetate, and perchlorate [4]. These counterions possess a relatively high basicity, which can be expressed by their ability to build up relatively strong hydrogen bonds toward acidic Brönsted groups [5].

Reactions of carbocations with silanol groups partially lead to covalent Si—O—C bonds [6], depending on the counterion employed [2]. However, according to Eq. (2), the degree of grafting not only depends on the concentration of the carbocation but also on the nature of the carbocation, the counterion, and the accessibility of the basic site of silanols. However, the basicity of the silanol oxygen atom appears to be relatively low according to Arnett's recent results [7]. Furthermore, it has been proposed that bromide as the counterion supports nucleophilic attack of the silanol oxygen atom upon the growing carbocation [2]:



We have found that the nature of the interaction between silica surface—OH groups and carbocation-ion pairs is difficult to explain; it is strongly dependent on both the basicity of the counterion and the steric geometry of the cation [5, 8, 9]. For instance, dissociated triphenylmethyl cation interacts only slightly with the silanol oxygen atom while the *p*-methoxybenzyl cation evidently interacts with silica [5, 8]. The objective of this paper is to investigate composite formation via the interfacial polymerization of *p*-methoxystyrene by *p*-methoxybenzyl cation-sulfate and -trifluoroacetate with silica as the initiator. Both these counterions possess a lower basicity than do the halide-silanol counterions reported on recently [2, 10].

EXPERIMENTAL

Materials

Aerosil (Degussa) and silica KG 60 (Merck) are commercial products. Prior to use, aerosil and KG 60 were heated for 12 h at 423 K and high vacuum so that BET surfaces of 278 and 300 m²/g, respectively, were obtained. Elemental analysis did not indicate traces of carbon on the surface of the silicas.

1,2-Dichloroethane was purified by standard procedures: it was dried over CaH₂ and freshly distilled before use.

p-Methoxystyrene was synthesized by the Grignard reaction from anisaldehyde and methylmagnesiumiodide according to Ref. 11, and it was dried over CaH₂.

p-Methoxybenzyl alcohol was synthesized by reduction of anisaldehyde with NaBH₄ and distilled in vacuum.

Procedure of Interfacial Polymerization

According to Ref. 1, the interfacial polymerization yields both extractable polymers with narrow molecular weight distributions and "living" oligo-*p*-methoxystyrene-hydrogen sulfate composites. The interfacial procedure was optimized to yield 90% composite with respect to monomer conversion [12].

The novel oligo-*p*-methoxystyrene-X⁻-silica composites were principally synthesized according to Scheme 1.

Fundamentally, the effective preparation of the interfacial initiator plays a key role. The silicas employed were evacuated for 12 h in Schlenk vessels at 423 K and then stored under argon before use. *p*-Methoxybenzyl alcohol was used as a solution in 1,2-dichloroethane under inert conditions. The heterogeneous mixture was stored in an ice bath for 2 h. The cointiating protonic acids, trifluoroacetic acid and sulfuric acid, were added slowly with vigorous stirring to the suspension. The mixture obtained was stored in the ice bath again for 6 h. The solid became pale pink in color.

The interfacial initiator yield was determined by elementary analysis and gravimetric measurements of the dried solids. The alcohol/acid ratio mainly influences the efficiency of the interfacial initiator as seen in Fig. 1 for trifluoroacetic acid and in Fig. 2 for sulfuric acid.

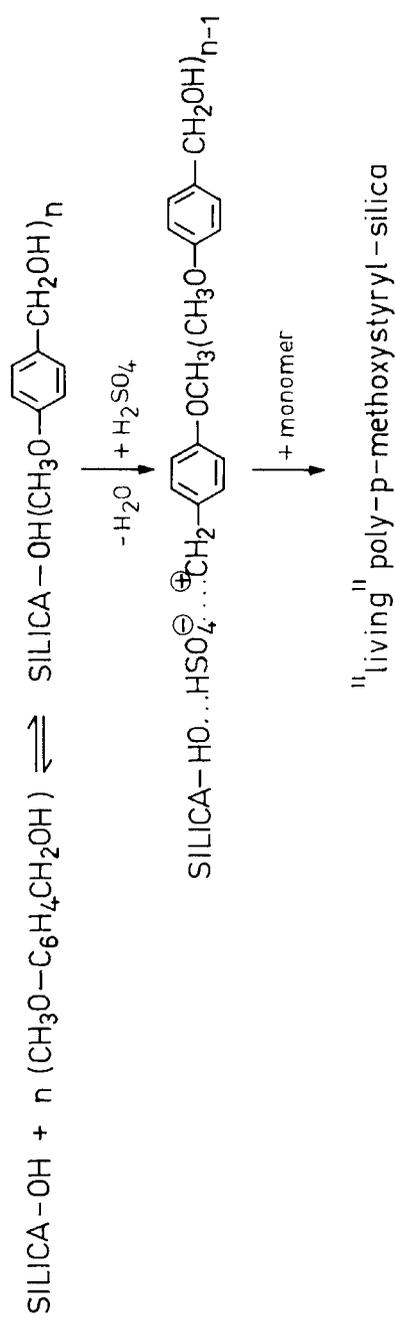
The decrease of the interfacial concentration of *p*-methoxybenzyl-trifluoroacetate with increasing trifluoroacetic acid concentration, as seen in Fig. 1, is due to complexation of the trifluoroacetate by the corresponding acid [13], Eq. (3). The adsorption of substituted acetic acids to form dimeric aggregates at silica surfaces according to Eq. (3) was previously reported by Rochester [14].



In the case of sulfuric acid, a higher acid concentration causes agglomeration of the particles. Hence, the synthesis of novel oligo-*p*-methoxystyryl-silica composites was carried out by using the optimized *p*-methoxybenzyl alcohol/protonic acid ratios: sulfuric acid/*p*-methoxybenzyl alcohol = 0.7 and trifluoroacetic acid/*p*-methoxybenzyl alcohol = 0.6. The addition of the *p*-methoxystyrene monomer was carried out directly after the preparation of the interfacial initiator. The solid adsorbate became a deep blue color within 2 minutes. The reaction goes to completion while storing the reaction vessel at 273 K for from 2 to 24 h. The crude product was separated by simple filtration, washed several times with 1,2-dichloroethane, and carefully dried in vacuum.

Solid-State ¹³C-NMR Spectroscopy

Solid-state ¹³C-NMR spectra were recorded by means of a home-built spectrometer (15 MHz, MAS, CP) from the Department of Physics in Jena as reported in Ref. 15.



SCHEME 1. Formulary scheme for the preparation of the cationically active oligo-*p*-methoxystyryl-hydrogen sulfate-silica composites.

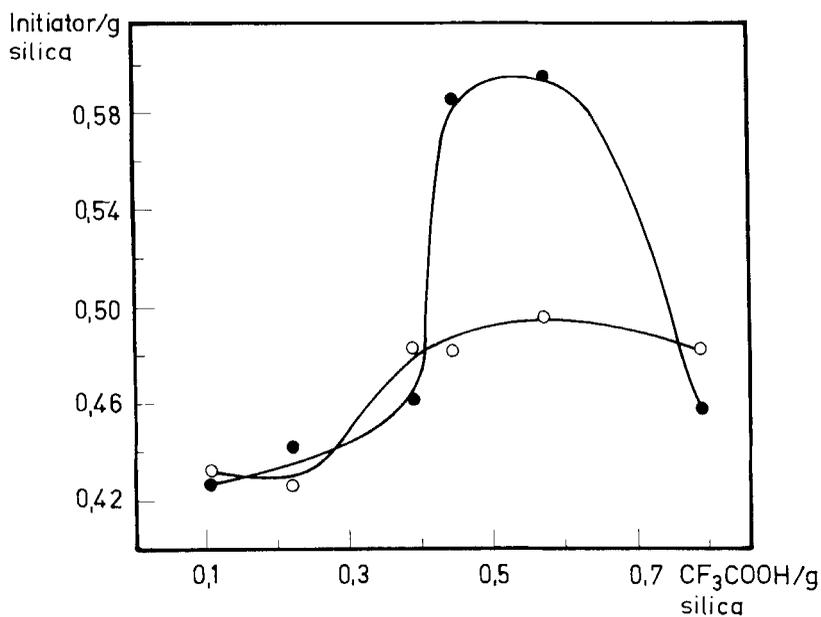


FIG. 1. Dependence of the yield of the interfacial initiator (as g per g silica) on the trifluoroacetic acid concentration at 273 K. Aerosil = 0.5 g, (○) *p*-methoxybenzyl alcohol = 0.11 g, (●) *p*-methoxybenzyl alcohol = 0.22 g.

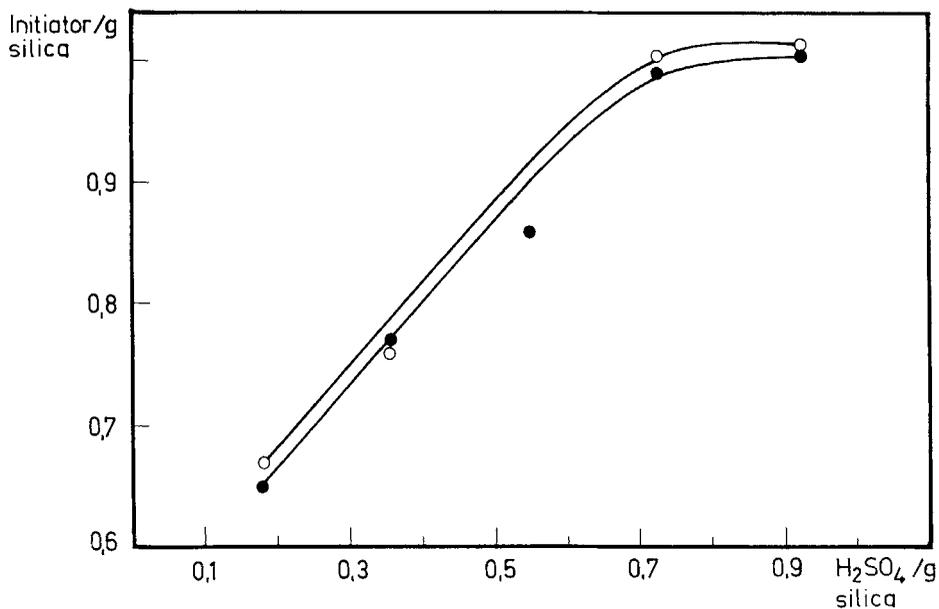


FIG. 2. Dependence of the yield of the interfacial initiator (as g per g silica) on the sulfuric acid concentration at 273 K. Aerosil = 0.5 g, (●) *p*-methoxybenzyl alcohol = 0.11 g, (○) *p*-methoxybenzyl alcohol = 0.22 g.

Zeta Potential Measurements

The electrophoretic measurements of the composites in aqueous KCl solution were performed by REPAP equipment as reported in Ref. 1.

UV/Vis Spectroscopy

The reflectance spectra were recorded on a Specord M40, Zeiss Jena, using a special disk for solid samples.

Electron Scanning Microscopy

The measurements were performed by Heinz Winkelmann, Department of Medicine, Friedrich Schiller University.

RESULTS AND DISCUSSION

In the case of *p*-methoxybenzylum-trifluoroacetate-silica initiation, the composites obtained involve mixtures of oligomers and polymers, and the entire carbon content in the new composite did not exceed 10% C. Unfortunately, the efficiency of the composite synthesis when applying trifluoroacetate as the counterion is rather low due to the enhanced formation of extractable polymers [12]. Thus, we will report exclusively on oligo-*p*-methoxystyryl-hydrogen sulfate-silica, which appears to be a material with outstanding properties. The novel composites have been characterized by means of elementary analysis, UV/Vis reflectance spectroscopy, solid-state ^{13}C -NMR spectroscopy, zeta potential measurements, and electron scanning microscopy.

The solid-state ^{13}C -NMR spectrum of oligo-*p*-methoxystyryl-hydrogen sulfate-silica is shown as Fig. 3. In addition to the expected signals at 100 . . . 150 and 30 . . . 40 ppm for the aromatic and aliphatic carbon atoms, a new signal appears at 66 ppm and is attributed to a covalent Si—O—C-bond as compared with $\text{Si}(\text{OC}_2\text{H}_5)_4$. Overlapping of this new signal with —OCH₃ units can be excluded by comparing the ^{13}C -NMR spectrum of poly-*p*-methoxystyrene ($\delta = 55$ ppm). In addition, the “living” oligo-*p*-methoxystyrene-hydrogen sulfate-silica possesses an intensive UV/Vis absorption with a maximum at $18,500\text{ cm}^{-1}$, which is due to an isomerized carbocation in the polymer chain according to Ref. 16 (compare Ref. 2). Surprisingly, the deep blue colored composite appears stable in the presence of water, but it decomposed rapidly in the presence of methanol or aqueous KOH. The corresponding UV/Vis spectra are shown in Fig. 4.

Elementary analysis (C, H, S) of the material, as represented in Figs. 3 and 4, indicates that the hydrogen sulfate concentration appears as a stoichiometric equivalency with respect to the oligomer chain ($M_n = 1000\text{ g/mol}$). Elementary analysis after treatment with KOH or methanol and further extraction of the products hints at sulfate traces remaining in the silica. A nucleophilic attack upon the carbocation linked at the surface by hydroxide or chloride or fluoride [1, 2] leads to unsaturated buta-1,3-diene end groups according to Ref. 17. The cationically “liv-

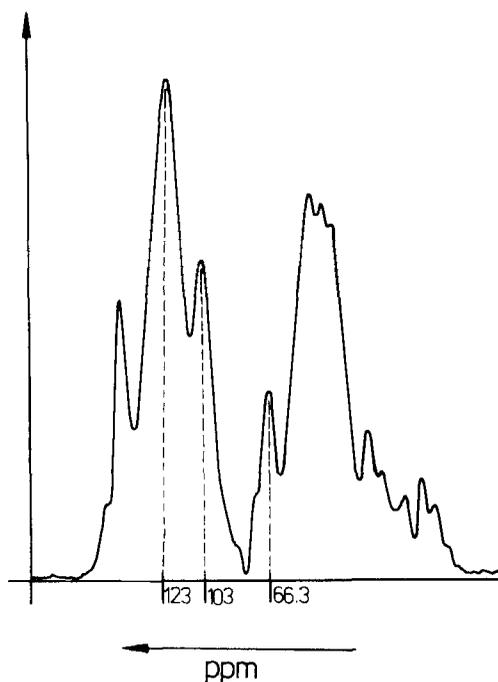


FIG. 3. Solid-state ^{13}C -NMR spectrum of a cationically "living" oligo-*p*-methoxystyrene-silica composite (16% carbon content).

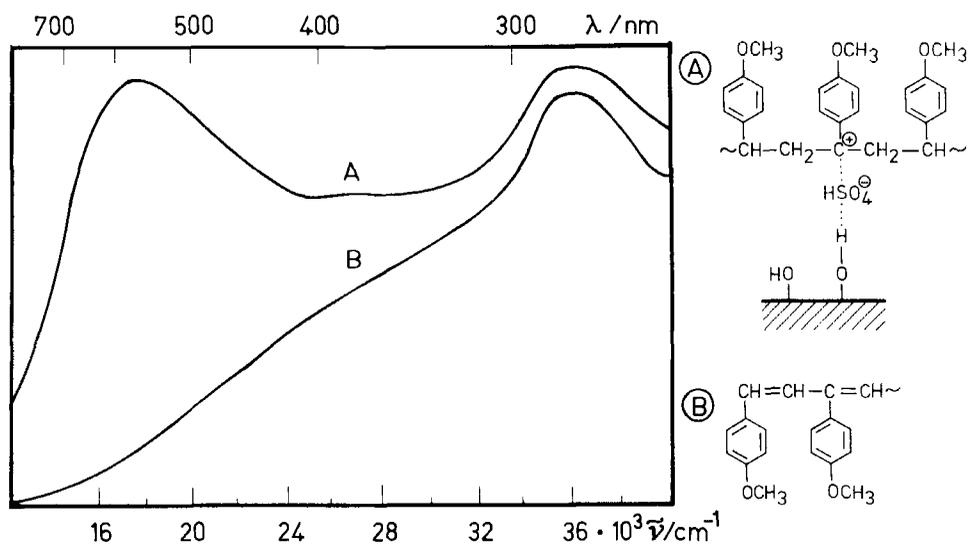


FIG. 4. UV/Vis reflectance spectra of oligo-*p*-methoxystyryl-hydrogen sulfate-silica ($M_n = 1000$ g/mol) obtained by interfacial polymerization with the following concentrations of the starting components: sulfuric acid = 0.5 mL, *p*-methoxybenzyl alcohol = 1.0 mL, silica = 10 g, and *p*-methoxystyrene = 3 mL. Carbon content of the composite = 15.3%. (A) Pure "living" composite, (B) after treatment with aqueous KOH.

ing" behavior of the novel composites, in comparison to bare silica-aerosil, can be demonstrated by zeta potential measurements in aqueous KCl solution (see Fig. 5).

In the interval from pH 0 to 7.0 (identified as Section A in Fig. 5 in comparison to the adequate UV/Vis spectrum of Fig. 4 in the same pH interval), the composite appears stable and no decolorization takes place. In this pH range the zeta potential plots are still reversible; they relate to changes of pH and ionic strength, i.e., the KCl concentration as the reference electrolyte. The course of the zeta potential plots as a function of the pH agrees well with the theory of cationically active surfactants in comparison to negatively charged surfactants, where the zeta potential plots have to be found as positive values [18, 19]. Basic media with a pH larger than 7.5 (identified as Interval B in Fig. 5) destroy the carbocation sphere of the composite, and this is accompanied by a large decrease in the zeta potential and decolorization as confirmed by the corresponding UV/Vis spectrum seen in Fig. 4 and Spectrum B which relates to Interval B in Fig. 5. The pale yellow materials obtained after pretreatment with aqueous KOH relate to properties close to those of the unmodified silica because they bear acidic silanol groups as seen from the zeta potential plots. It is obvious that the zeta potential values of the cationically active composite in the plateau range from pH 3 to 7.0 depend on the ionic strength of the medium. Hence, the adsorption of chloride ions onto cationically active polymer chains coordinated at surface groups causes the formation of an electrochemical double layer due to the specific interaction of the chloride [18].

Electron scanning microscopic investigations gave rise to the suggestion that closed particles, which are included in the polymer matrix, are responsible for the

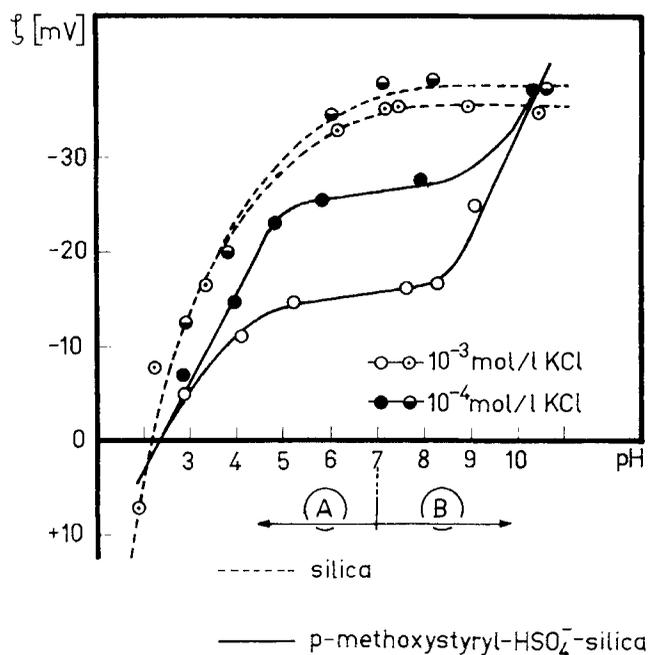


FIG. 5. Zeta potential plots of a cationically active oligo-*p*-methoxystyryl-silica composite and their dependence on the pH strength of the aqueous media. The zeta potential plots are related to the spectra in Fig. 4; the same sample has been measured.

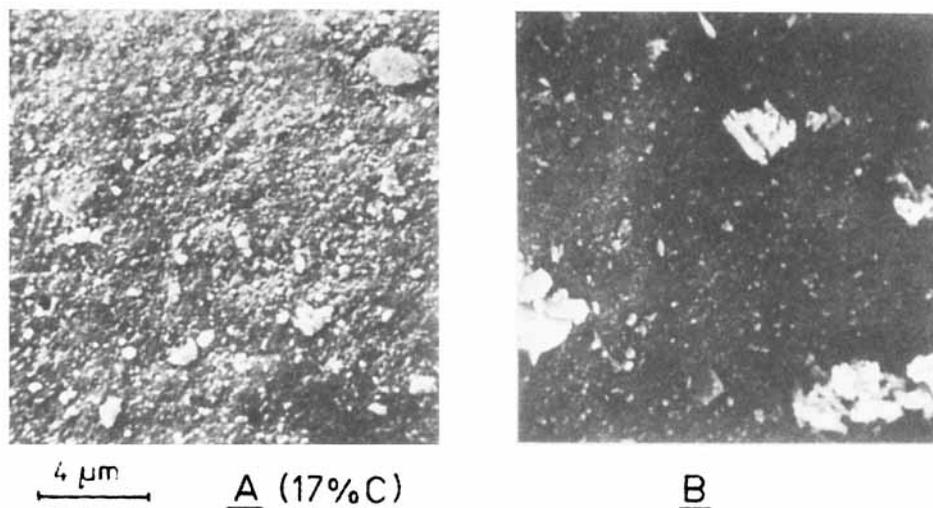
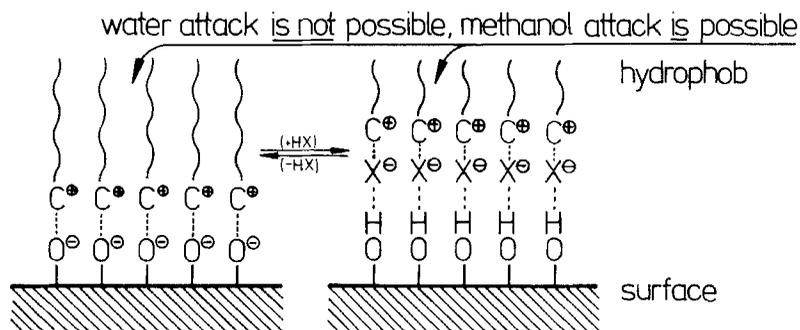


FIG. 6. Electron scanning micrographs of a cationically living composite (A) and of the same composite after treatment with a methanolic KOH solution (B).

outstanding water resistance of the supported carbocations as reported in this article (see Fig. 6). It is suggested that the hydrophobic chains are opposite to the liquid phase, which prevents the attack of nucleophilicities as water or chloride, while the carbocation is close to both the surface—OH groups and the counterion. This is confirmed by the gradual disappearance of the single silanol-valency vibration at 3740 cm^{-1} as measured by FTIR spectroscopy according to Refs. 20 and 21. The detection of a covalent Si—O—C bond by IR spectroscopy was not possible due to the strong absorption of hydrogen sulfate in the same region as the Si—O—C valency vibration appeared [2]. A similar explanation is given for the hydrolytic stability of the Si—O—R bond toward aqueous protonic acids. The chain length of the grafted alkyl groups—R determines its stability due to the suppression of the hydrophilic attack of water upon the Si—O—C bond [22, 23].

Finally, the Scheme 2 model is proposed to explain the experimental results.



SCHEME 2. Proposed model for the explanation of the water resistance of the oligo-*p*-methoxystyryl-hydrogen sulfate-silica composites.

CONCLUSION

The results show that hydrogen sulfate is a convenient counterion for the preparation of cationically active polymers on silica surface groups.

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