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# SPECTROSCOPIC INVESTIGATION OF SOLID POLY-*p*-METHOXYSTYRENE–AEROSIL COMPOSITES OBTAINED BY TRIPHENYLMETHYLIUM–HALIDE–AEROSIL INITIATION

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## ABSTRACT

The composites of poly-*p*-methoxystyrene and aerosil obtained by interfacial initiation with triphenylmethylium–halide–aerosil have been investigated by the BET method, UV/Vis spectroscopy, FTIR spectroscopy, thermogravimetry, and elementary analysis. In the case of triphenylmethylium–bromide–aerosil initiation, cationically active composites are obtained which have covalent Si—O—C bonds. The structures of the polymer–aerosil bonds are discussed in comparison with results obtained from model compounds.

## INTRODUCTION

In the previous article on this subject we reported on the soluble polymer fractions (extractable by cold solvent) obtained by cationic interfacial polymerization of *p*-methoxystyrene by triphenylmethylium–halide–aerosil initiation [1]. In addition to the formation of extractable polymers, new composites of poly-*p*-methoxystyrene and aerosil were obtained [2]. The yield ratio of both composite and extractable polymers can be controlled by the concentration of the starting monomer and initiator, as reported in detail in Ref. 1. Dissociated triphenyl-

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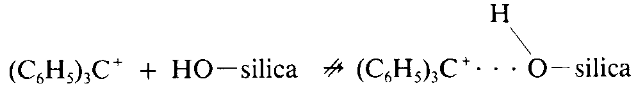
methylium evidently does not interact with silanol surface groups (Eq. 1) due to steric hindrance [3, 4].



$$(C_6H_5)_3C^+ + HO{-}silica \not\rightarrow (C_6H_5)_3C^+\cdots \overset{H}{O}{-}silica \qquad (1)$$

However, the interaction of growing chain ends with surface groups can sometimes produce composites, according to Ref. 5.

Further model reactions show that the reactivity of the bis-4,4-(methoxyphenyl) methylium, which possesses a closed electrophilicity (expressed as $pK_{R^+}$) to triphenylmethylium, is 1,000,000 times larger toward olefins than the triphenylmethylium [6]. This example confirms the influence of steric effects by taking into account the reaction of carbocations. The role of steric effects in adsorption processes in comparison to electronic influence is reported in detail by Arnett et al. [7, 8].

However, it was established that cationic interfacial polymerization yields both extractable polymers with narrow MWDs and composites. This paper investigates composite formation and the nature of the bonds between the polymer and the silica surface by means of FTIR spectroscopy and other methods.

## EXPERIMENTAL

### Materials

The composites were obtained by cationic interfacial initiation as reported in Refs. 1 and 2. The crude composites were carefully dried and stored in a glass vessel under argon. The degree of grafting was determined by two independent methods: elementary analysis and gravimetry. The formation of poly-*p*-methoxystyrene-aerosil composites was additionally confirmed by thermogravimetric analysis as shown in Fig. 1.

The qualitative courses of the thermogravimetric plots of two selected composites and of a pure poly-*p*-methoxystyrene sample agree. This supports the formation of the assumed polymer layer. This is confirmed by the decrease in the specific surface area, which depends on the polymer content of the poly-*p*-methoxystyrene-aerosil composite expressed as % C, as shown in Fig. 2.

### FTIR Spectroscopy

The IR-solid-state spectra were recorded by a Fourier transform infrared spectrometer IRF 180 (Zentrum für wissenschaftlichen Gerätebau der AdW der ehemaligen DDR) with a resolution of 4 $cm^{-1}$ and a scanning period of 200 scans. The diffuse reflectance spectra were obtained by placing a diffuse reflectance accessory in the sample chamber. The spectra of the samples were divided by the pure KCl spectrum. The intensity units are expressed as Kubelka-Munk units.

The transmission spectra were carried out by pressing the samples (3.0-4.0 mg) into 20 mm disks.

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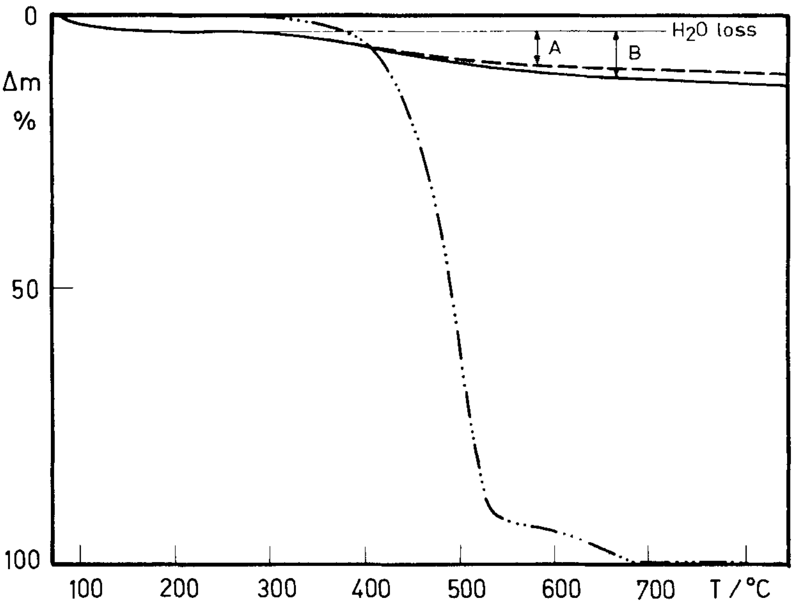

FIG. 1. Thermogravimetric results of two selected composite samples in comparison to a pure poly-*p*-methoxystyrene sample. (——) B, 9.6% C; (- -) A, 5.1% C; (· · · —) poly-*p*-methoxystyrene.

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## UV/Vis Spectroscopy

The UV/Vis spectra were carried out with a SPECORD M40, Carl Zeiss Jena, using a special disk for reflectance measurements.

## Measurements of the BET Surface Area

The change of the aerosil surface in the course of cationic interfacial polymerization was characterized by measurements of the BET surface area.

# RESULTS AND DISCUSSION

As reported in Ref. 1, triphenylmethylium-halide-aerosil initiation yields different composites depending on the counterion employed. In the case of triphenylmethylium chloride- and fluoride-aerosil initiation, dormant polymer-aerosil composites are obtained which have a yellow color due to unsaturated end groups, as shown in the UV/Vis spectrum of Fig. 3.

The unsaturated end groups are formed by proton abstraction from an allylium cation upon the nucleophilic counterions (fluoride and chloride) according to the mechanism discussed by Gandini and Plesch [9] for the case of styrene polymerization by perchloric acid. The IR spectra confirm the formation of conjugated double bonds in the polymer chain. However, the composite synthesis carried out by triphenylmethylium initiation with chloride and fluoride as counterions is

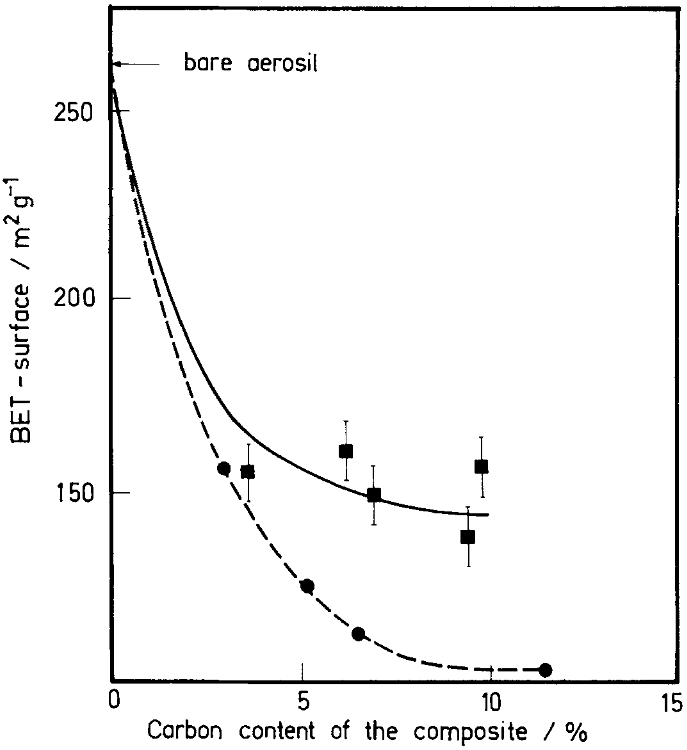

FIG. 2. Decrease of the BET surface area depending on the carbon content (% C) of poly-*p*-methoxystyrene-aerosil composites. (■) In the case of triphenylmethylium chloride or fluoride-aerosil initiation, mainly oligomer fractions are obtained. (●) In the case of triphenylmethylium-bromide-aerosil initiation, mainly polymers—$M_n$ = 4000 g/mol—are formed.

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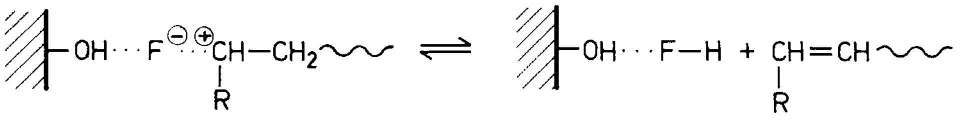
unsatisfactory. This is confirmed by the random coverage of the surface of the aerosil by the oligomers obtained, as seen from the decrease of the BET surface area (see Fig. 2). HX is formed by proton abstraction from the chain end which can interact simultaneously with nonadsorbed triphenylmethylium halide [10] as shown by



$$\text{—OH}\cdots\text{F}^{\ominus}\cdots{}^{\oplus}\underset{\text{R}}{\text{CH}}\text{—CH}_2\sim\sim \rightleftharpoons \text{—OH}\cdots\text{F—H} + \underset{\text{R}}{\text{CH}}\text{=CH}\sim\sim \qquad (2)$$

$$(C_6H_5)_3CF + HF \rightleftharpoons (C_6H_5)_3C^{\oplus}HF_2^{\ominus}$$

Thus, the desired condition for exclusive interfacial polymerization, which requires that the species in solution are inactive during initiation, is not accom-

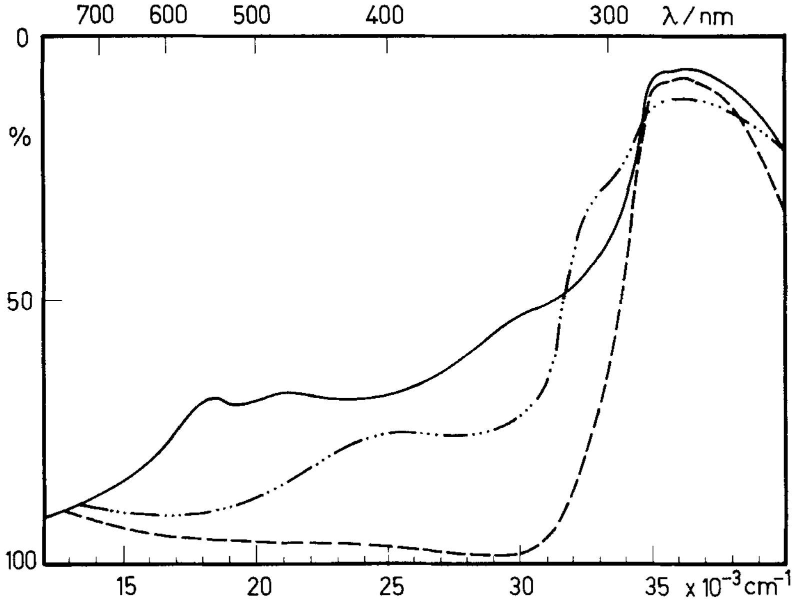


FIG. 3. UV/Vis reflectance spectra of poly-*p*-methoxystyrene-aerosil composites: (——) by means of triphenylmethylium-bromide-aerosil initiation (composite contains 10.8% C); (· · · —) by means of triphenylmethylium-chloride-aerosil initiation (composite contains 11% C); (- -) pure poly-*p*-methoxystyrene was adsorbed at aerosil (10% C).

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plished. Furthermore, we could show that the efficiency of composite synthesis strongly depends on the triphenylmethylium halide concentration, as is qualitatively confirmed by the zeta potential plots of triphenylmethylium halide-aerosil in 1,2-dichloroethane. Figure 4 shows a qualitative comparison of zeta potential plots and of composite formation yield as it depends on the overall initiator concentration.

In accord with the plots in Fig. 4, we propose that the composite formation preferably takes place in the so-called Stern layer while the extractable polymers are formed mainly in the diffuse layer [1]. Therefore, the Stern layer is defined as a chemisorbed layer which is in direct contact with the surface of the solid while the diffuse layer is mobile and in weak contact with the Stern layer. This corresponds to established colloid chemical phenomena [11]. In the case of bromide-aerosil as the "counterion," the plots agree with respect to the overall initiator concentration; in the case of fluoride-aerosil, the composite formation takes place at a lower initiator concentration in relation to the zeta potential frontier. This is due to the observed proton transfer on the fluoride after monomer addition according to the above scheme. This means that HF and HCl, respectively, are formed immediately, further influencing the reaction steps due to $HX_2$ formation. In this case, the simultaneous formation of $(C_6H_5)_3C^+HX_2^-$ is responsible for the shift of the ionization barrier as indicated by the decrease in the essential concentration which starts the composite formation in comparison to the overall triphenylmethylhalide. Unfortunately, higher initiator concentrations cause broader MWD curves, and higher initi-

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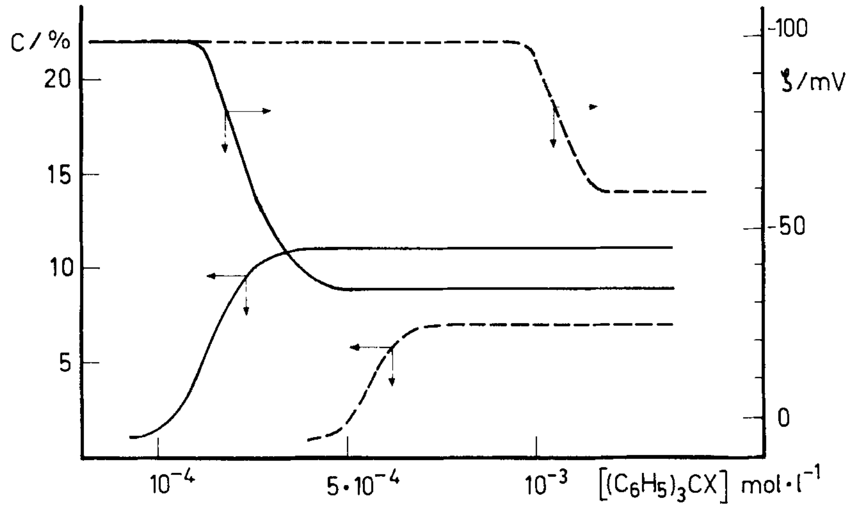

FIG. 4. Comparison of composite yield (% C) and zeta potential plots of two triphenylmethylium-halide initiators and the dependence on the overall triphenylmethyl halide (X) concentration (according to Ref. 1): (- -) X = F; (——) X = Br.

ator concentrations drastically enhance composite formation, which leads to a significant deterioration of the surface activity of the coinitiating solid. If higher initiator concentrations are present, the interfacial polymerization increasingly occurs in the diffuse "layer" of the solid-liquid interface [1].

This means that the more distant the ion pair is from the acidic surface, the more proton transfer will take place upon the counterion due to the increased basicity of the free halides. However, as seen in Fig. 3, the UV/Vis spectrum of the poly-*p*-methoxystyrene-aerosil obtained by triphenylmethylium-bromide-aerosil initiation possesses three UV/Vis maxima which are attributed to three kinds of "living" poly-*p*methoxystyryl species, as known from the literature [12, 13]. The specification of this initiating system, which approaches living conditions, is confirmed by adequate Szwarc plots as reported in Ref. 1. The UV/Vis maxima are attributed to the species shown in Scheme 1.

The appearance of different kinds of carbocationic species growing in the course of cationic polymerization is discussed as a multiplicity of the propagating species as suggested for *p*-methoxystyrene [14]. However, the specific detection of the different carbocationic species formed is not possible in solution at room temperature due to the high cationic reactivity of the *p*-methoxystyrene monomer. Advantageously, the adsorption of living ion pairs onto acidic surface groups allows their simultaneous investigation by means of UV spectroscopy. This means that the coordination onto acceptor surface groups acts like a frozen matrix, as suggested by Leftin [4].

The IR spectrum of the poly-*p*-methoxystyryl-aerosil composite clearly indicates the disappearance of the single Si—OH vibration at 3740 $\text{cm}^{-1}$ (see Fig. 5).

In comparison with the ionic adsorbate, $(4\text{-}CH_3OC_6H_4)_2(C_6H_5)C^+Cl^- \cdots$

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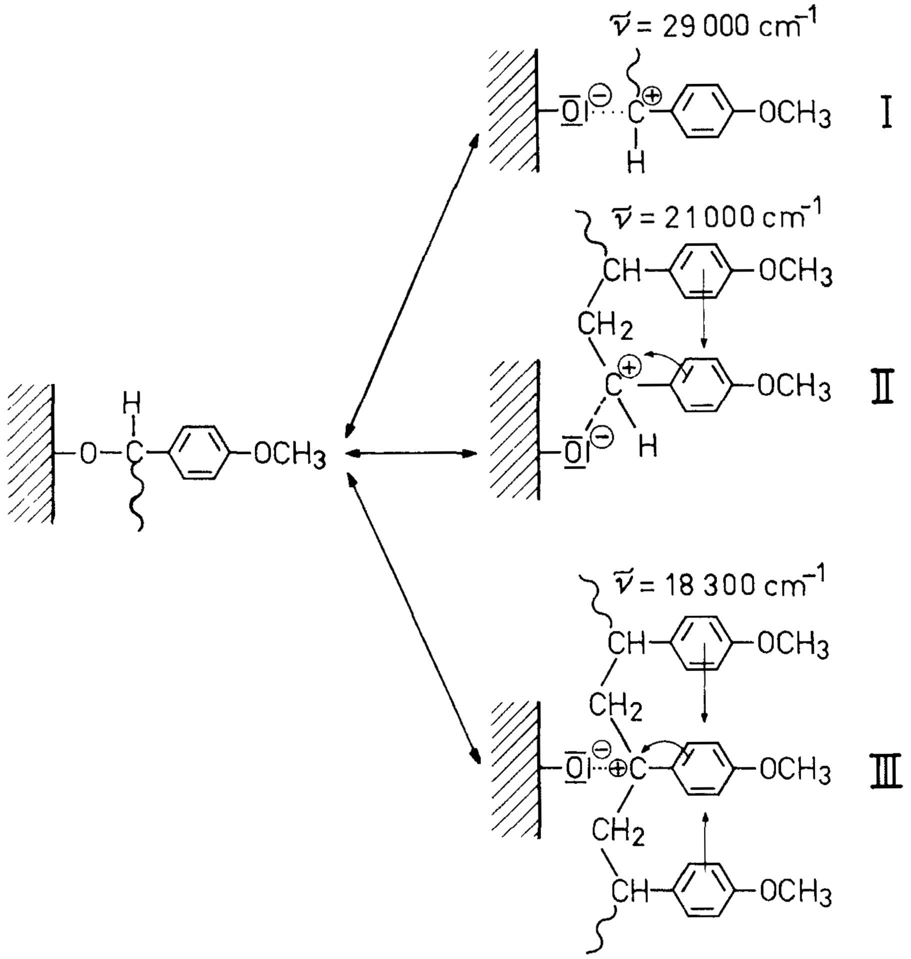

different kinds of poly-p-$CH_3O$-styryl-silica obtained by means of $(C_6H_5)_3CBr$-aerosil initiation

SCHEME 1.

HO-aerosil, where the silanol group undergoes only a weak interaction, the decrease of the single Si—OH vibration is less important (Fig. 5).

In the latter case the associated Si—OH vibration is shifted to lower energies due to the increase of the SiO—H bond length (see Fig. 6) according to Refs. 15 and 16. In comparison, water is less adsorbed than the interfacial ion pair, as seen from the lower shift of the Si—O—H vibration in Fig. 6.

In the difference FTIR spectrum of the aerosil-poly-*p*-methoxystyrene composite and the bare aerosil, as shown in Fig. 7 in the range from 800 to 1200 cm$^{-1}$, a new signal appears at 953 cm$^{-1}$. It is attributed to a Si—O—C valency vibration, in

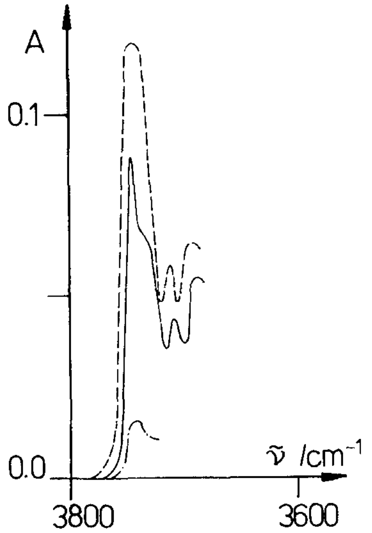

FIG. 5. IR reflectance spectra of aerosil-carbenium adsorbates: (——) (4-$CH_3OC_6H_4)_2(C_6H_5)C^+ \cdots Cl^- \cdots$ HO-aerosil; (- · -) poly-*p*-methoxystyrene-aerosil composite obtained by triphenylmethylium-bromide-aerosil initiation (10.8% C); (- -) aerosil after dehydration.

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agreement with other authors [17, 18] and in comparison with the model compound $Si(OC_2H_5)_4$.

Elementary analysis shows only traces of halogen. That means a reaction takes place between the cationic chain ends and silanol groups to produce a covalent Si—O—C bond in the formation of living adsorbed polymers.

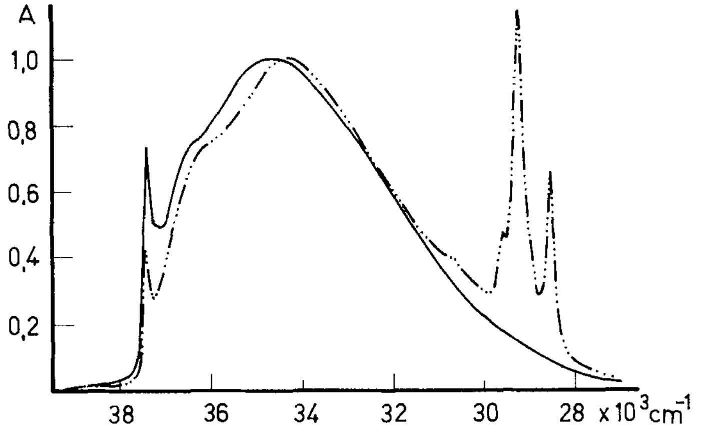

FIG 6. IR transmission spectra of bare aerosil (——) and the ionic adsorbate aerosil-OH $\cdots Cl^- \cdots C^+(C_6H_5)(4\text{-}CH_3OC_6H_4)_2$ (4.3% C) (· · · —).

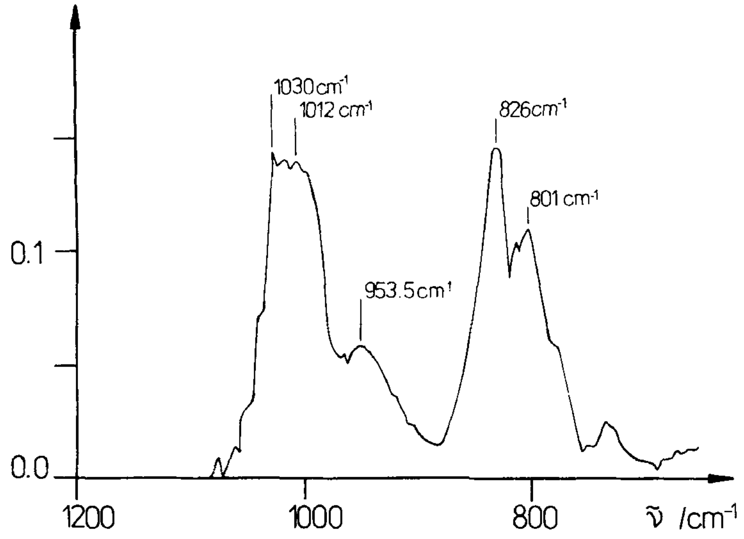

FIG. 7. FTIR difference spectrum of the cationically active poly-*p*-methoxystyrene-aerosil composite (measured by the reflectance technique).

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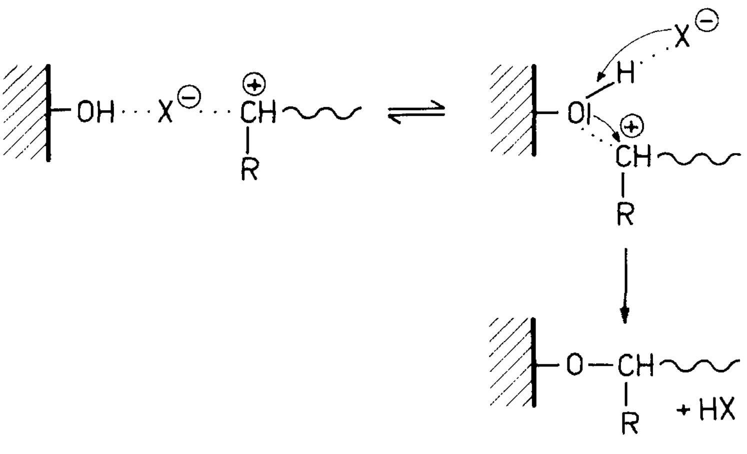
Silica surfaces have a very low basicity, as reported recently by Arnett [19]. This is confirmed by the low donicity [20]. For that reason, we recommend the procedure demonstrated in Scheme 2.

A nucleophilic attack of the counterion upon the silanol causes an increase of the basicity of the silanol oxygen due to the supposed coordination model. This is followed by a drastic lowering of the basicity of the anions which are in contact with acidic surface groups [21] as well as by an increase of the acidity of adsorbed weak Brönsted acids [22] according to established acid-base theories which take into account self-complexation of the corresponding counterion [23].



SCHEME 2.

## CONCLUSION

The results of cationic interfacial polymerization of *p*-methoxystyrene at silica show that the composite formation is strongly influenced by the counterion employed. In the cases of chloride and fluoride as counterions, proton transfer upon the growing chain end plays the main role, which is disadvantageous for the composite properties. Bromide as a counterion prefers the formation of cationically living polymers and composites which have covalent Si—O—C bonds.

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