Cationic Interracial Polymerization of *p*-Methoxystyrene by Means of Triphenylmethylium Halide-Aerosil Initiation

Stefan Spange[a]; Günther Heublein[a]; Frank Simon[a]

[a] Institute of Organic and Macromolecular Chemistry Friedrich Schiller University of Jena Humboldstrasse 10, Jena, German Democratic Republic

PLEASE SCROLL DOWN FOR ARTICLE

CATIONIC INTERFACIAL POLYMERIZATION OF p-METHOXYSTYRENE BY MEANS OF TRIPHENYLMETHYLIUM HALIDE—AEROSIL INITIATION

STEFAN SPANGE,* GÜNTHER HEUBLEIN,† and FRANK SIMON

Institute of Organic and Macromolecular Chemistry
Friedrich Schiller University of Jena
Humboldstrasse 10, Jena, GDR-6900, German Democratic Republic

ABSTRACT

Cationic polymerizations of p-methoxystyrene initiated by triphenylmethylium halides in conjunction with silica surfaces proceed via ion pair intermediates. The polymerization yields both aerosil-polymer composites and soluble polymers. The triphenylmethylium halides are active only on the surface of the solid, which is demonstrated by means of adsorption and zeta-potential measurements in 1,2-dichloroethane. The influence of the overall monomer concentration and initiator concentration on the MWD curves and composite formation is discussed in relation to the mechanism of cationic polymerization. Triphenylmethylium bromide–aerosil adsorbates yield soluble polymers with narrow MWD curves ($M_w/M_n \simeq 1,2$). This behavior approaches living conditions. The formation of composites mainly proceeds in the Stern layer of the ion pair layer which covers the aerosil particle while the generation of soluble polymers occurs in the diffuse layer. The behavior of interfacial polymerization is discussed in relation to surface chemistry and the mechanism of cationic polymerization. A general model

†Deceased. See page 394.

for interfacial polymerization is proposed for triphenylmethylium halide–aerosil initiation.

1. INTRODUCTION

After the discovery of pseudocationic polymerization by Gandini and Plesch [1], many advantages of long-living cationic vinyl polymerization processes have been put forward [2–4]. The wide field of pseudocationic polymerization has been discussed intensively during the past few years [5–7] because long-living chain carriers or chain ends capable of reactivation [8] are relevant for the application of cationic vinyl polymerization [9]. The interaction of carbocations with nucleophilic counterions in the course of propagation is an important factor suppressing side reactions such as transfer to the monomer. It is generally established that the lower the potential energy of the active chain carrier, the narrower the MWD [5].

The formation of activated esters, as one kind of reactive species, strongly depends on the conditions for the polymerization [10, 11]. According to the thermodynamic equilibrium (Eq. 1), the formation of ion pairs is connected with the presence of dissociated ions. The latter usually possess relatively high reactivities in the course of propagation, and, as a result, broad MWD curves of the polymers are obtained.

$$R-X \underset{K_i}{\rightleftharpoons} R^+X^- \underset{K_d}{\rightleftharpoons} R^+ + X^- \qquad (1)$$

The overall constant is given as $K_{Br} = K_i K_d$, and if K_d or K_i becomes zero, no ionized species are relevant [12]. Ionization processes (K_i) of polarized carbon—halogen or carbon—oxygen bonds strongly depend on the experimental conditions, and the differences of free energy between the different species participating in the ionization process can be very low [5, 11]. Many counterions which can form esters, such as picrate [13], ClO_4^- [14], NO_3^- [15], and CF_3COO^- [10, 11, 16], have been considered. However, increasing nucleophilicity of the counterion suppresses transfer to the monomer and enhances proton removal from the active species by the counterion (see Eq. 2).

$$\sim CH_2-\underset{\underset{R}{|}}{CH^+} + X^- \rightleftharpoons \sim CH=\underset{\underset{R}{|}}{CH} + HX \tag{2}$$
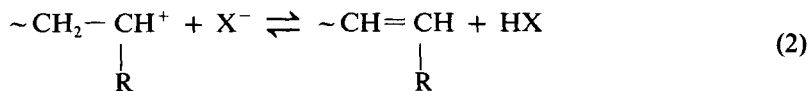
During polymerization, the HX formed can act simultaneously in initiation or counterion complexation (Eq. 3) depending on concentration and the nature of monomer and initiator, respectively.

$$\sim CH_2-\underset{\underset{R}{|}}{CH^+}\ X^- + n\text{-}HX \rightleftharpoons \sim CH_2-\underset{\underset{R}{|}}{CH^+} + X(HX)_n^- \tag{3}$$
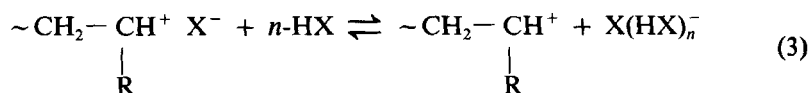
This behavior has been very well established for halides and picrate counterions [13, 17]. Acceptors of moderate strength, such as silica [18, 19], do not initiate the polymerization of p-methoxystyrene, but they are capable of coordination of halide counterions [8]. The adsorption of triphenylmethyl chloride, bromide, and fluoride on silica proceeds with ioniza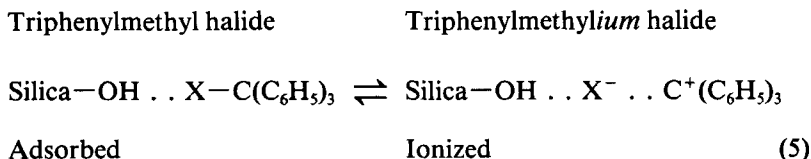tion of the carbon—halogen bond via hydrogen bonding (see Eq. 4). Consequently, counterion stabilization may be due to the formation of interfacial ion pairs as illustrated by

$$\text{Silica}-OH + Cl-(C_6H_5)_3 \rightleftharpoons \text{Silica}-OH \ .\ .\ Cl^- \ .\ .\ C^+(C_6H_5)_3 \tag{4}$$
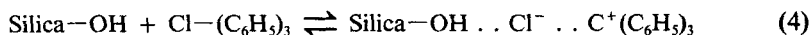
According to Arnett's review [8], it is suggested that ionization predominantly occurs via different kinds of silanol groups because the d-orbitals of silica do not play an important role in the course of donor attack upon silica surfaces. Common electrolytic dissociation processes in the bulk phase cannot take place due to ion recombination during the desorption of ionized triphenylmethyl halides. Thus, the supernatant liquid above the colored, solid adsorbates appears colorless if traces of water have been carefully excluded [20]. It is known that ion recombination of triphenylmethylium with halides in 1,2-dichloroethane solution takes place as a diffusion-controlled process [21]. In contrast, the adsorption of carbenium ion pairs onto silica surfaces allows an exclusive interfacial initiation by means of triphenylmethylium halide-silica in inert liquids like 1,2-dichloroethane [8].

Further, the adsorption equilibria of halides on silica surfaces might afford a new means of investigating propagating species which exclusively involve ion pairs and activated carbon—halide bonds according to Eq. (5). The following classification of interfacial species may be used:

Triphenylmethyl halide   Triphenylmethyl*ium* halide

$$\text{Silica}-\text{OH} \ . \ . \ \text{X}-\text{C}(\text{C}_6\text{H}_5)_3 \ \rightleftharpoons \ \text{Silica}-\text{OH} \ . \ . \ \text{X}^- \ . \ . \ \text{C}^+(\text{C}_6\text{H}_5)_3$$

Adsorbed   Ionized   (5)

A more detailed electrokinetic and adsorption measurement study concerning the influences of the structural parameters of triphenylmethyl derivatives, such as the ring substituents and the nature of X^- on the equilibrium in Eq. (5), is reported in Ref. 23. The objective of this paper is to determine the suitability of interfacial polymerization for the synthesis of new polymers. *p*-Methoxystyrene has been used as the monomer because initiation by triphenylmethylium is well established [22].

We also report on the mechanism of interfacial polymerization by means of adsorption measurements, electrokinetic measurements, GPC, and other methods.

EXPERIMENTAL

Materials

Aerosil is a commercial product (Degussa, Frankfurt/Main). Prior to use, aerosil was heated for 12 h at 423 K under high vacuum so that a BET surface of 278 m^2/g and an acceptor number (AN) of 53 could be obtained [19]. Elemental analysis does not indicate traces of carbon on the surface of the aerosil.

1,2-Dichloroethane was purified by standard procedures; it was dried over CaH_2 and freshly distilled before use. Additionally, aerosil was used as a drying agent for the applied liquid, especially when very low initiator concentrations were used (below 5×10^{-4} mol/L with respect to the overall bulk).

p-Methoxystyrene was synthesized by the Grignard reaction from anisaldehyde and methylmagnesiumiodide according to Ref. 24, and dried over CaH_2.

The triphenylmethyl halides were prepared from triphenylmethyl alcohol and the corresponding acetyl halide according to Ref 25.

Procedure of Interfacial Polymerization

All experiments were carried out in a dry argon atmosphere. Aerosil was dried directly in the reaction vessel. In every case, 500 mg of aerosil

was used, and the concentrations given are with respect to the overall bulk including the aerosil and the solvent. The monomer was added with a syringe. The polymerization was initiated by the addition of freshly prepared stock solutions of the triphenylmethyl halide or p-methoxystyrene. The two methods applied are described in the Results Section.

The carbenium species were formed on the aerosil surface immediately after the addition of the triphenylmethyl initiator. The volume phase above the aerosil must remain colorless. In the presence of water, when aerosil was used without dehydration, the bulk phase appears pale yellow due to hydrolysis products. In the latter case, many competing reactions must be taken into account. For instance, the presence of water increases the M_w/M_n ratio of the extractable polymers and decreases the number of reactive polymer chains on the aerosil surface as seen from the data in Table 1.

This is due to two effects of water. The increase of the M_w/M_n ratio is due to suppression of the propagation reaction, and the decrease in the chemical bonding polymer is due to disruption of contact of the aerosil surface with the propagating species. During interfacial polymerization, the aerosil becomes turbid between 5 and 60 min after initiation depending on the reaction conditions; this is caused by physically adsorbed and chemically bonded polymers. Therefore, measurement of the time-dependent concentration of triphenylmethylium was not possible by means of UV spectroscopy during interfacial polymerization in suspension.

Polymerization was stopped by rapidly filtering off the aerosil solid. The crude aerosil adsorbates were extracted several times with 1,2-dichloroethane at room temperature, and the combined extracted polymer fractions were precipitated in methanol and purified by standard

TABLE 1. Influence of the Preparation Conditions of Aerosil on the Properties of Soluble Polymer Fractions Obtained by Means of $(C_6H_5)_3C^+Cl^-$–Aerosil Initiation at 273 K

Preparation condition	M_n, g/mol	$\overline{M}_w/\overline{M}_n$	% C (composite)
Without drying	8,600	4.4	3–4
6 h at 673 K under vacuum	22,000	1.25	12.5
12 h at 413 K under vacuum	22,000	1.3	12.0

procedures. The aerosil composites were dried over CaH_2 and paraffin in vacuum. The elemental analyses of the composites were of good reproducibility and were confirmed by thermogravimetric analysis and gravimetric results.

Quantitative Adsorption Measurements

Aerosil (500 mg) was prepared as reported above, and a stock solution of p-methoxystyrene in 1,2-dichloroethane was placed in the reaction vessel. The sample was mixed by ultrasonic treatment for 10 min. The vessels were stored in a thermostat for 6 h, and the concentration of the supernatant solution was dependent on both the reaction time and the overall concentration of p-methoxystyrene. The concentrations were determined by means of UV spectroscopy in the range from 40,000 up to 32,000 cm^{-1} in relation to the stock monomer solution. Gas chromatography gave the same results. A similar procedure was used for the triphenylmethyl derivatives [23].

Zeta-Potential Measurements

The zeta potential of the solid–liquid interface was determined by means of electrophoretic methods. The zeta potential is given by the Henry equation [26]:

$$\zeta = \frac{3U_E\eta}{2f(\kappa,a)\epsilon_0\epsilon_r} \tag{6}$$

where η = viscosity of the solvent (liquid)
ϵ_r = dielectric constant of the liquid
ϵ_0 = influence constant
$f(\kappa,a)$ = ratio between particle diameter and thickness of the diffuse flayer
U_E = electrophoretic mobility = V_v/E
V_p = rate of the particle influenced by the electric field
E = electric field strength

For aerosil–1,2-dichloroethane, the following condition is valid: $\kappa \cdot a \gg 1$, which means that $f(\kappa,a) = 1$ [27]. The electrophoretic mobility was determined by means of Repap zeta-potential equipment. The closed
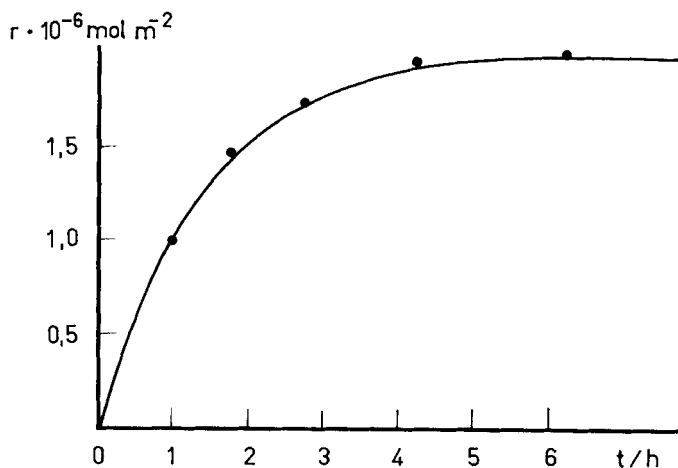
$r \cdot 10^{-6} mol \, m^{-2}$

FIG. 1. Time-dependent adsorption of p-methoxystyrene onto the aerosil surface of the 1,2-dichloroethane mixture, $T = 298$ K, [M] = 0.075 mol/L.

cell included two Pt electrodes separated by a distance of 0.9 cm. The separation distance of the glass windows was 0.1 cm. The electric field strength for measuring the zeta potential was in the order of 100 V/cm. The suspensions were prepared as described above. Every zeta-potential value was determined by 10 independent measurements. The error of the reported values was of the order of 5%.

RESULTS OF INTERFACIAL POLYMERIZATION

There are two principal methods of experimentation for carrying out interfacial polymerizations:

Method A: The monomer is dispersed in the solid–liquid mixture and the initiator is added as solution at a specific concentration to this mixture. The adsorption equilibrium of monomer–silica in 1,2-dichloroethane appears constant after 6 h (see Fig. 1). In every case the addition of initiator took place after 6 h.

Method B: First, the triphenylmethylium halide–aerosil adsorbate is prepared in the reaction vessel, and after this the monomer is added by

means of a syringe. It is noteworthy that the colorless liquid phase above the solid initiator is completely inactive for initiation.

Interfacial polymerization carried out by both experimental methods is strongly time-dependent and is also related to adsorption equilibria of monomer/silica, polymer immediately formed/silica, and triphenyl-methylium halide/silica which permanently influence the surface concentrations. This is due to competing adsorption of the active species, the monomer, and the polymer. The solid aerosil initiator contains varying amounts of oligomers and polymer in every case after monomer conversion. This result suppresses interfacial polymerization relative to the initiator effectiveness. It is well known from the heterogeneous catalysis of isobutene polymerization [28, 29] that the polymer generated covers the silanol groups at the silica surface. The requirement of silanol groups supporting the active species at the silica surface excludes the mechanism known from heterogeneous catalysis. The mechanism of pseudocationic and reactivation polymerization does not explain the experimental results [2, 8]. For instance, comparison of the combined polymer fractions obtained by triphenylmethylium chloride–aerosil initiation carried out by Method A is shown in Fig. 2.

The unextracted amounts of polymers were isolated by treating the aerosil composite with 40% aqueous HF or 20% aqueous KOH solution, followed by extraction of the reaction mixture with benzene. The choice of solvent has no significant influence on the MWD curves of the unextractable fractions chemically bonded on aerosil, indicating no side reactions. The mass of the unextractable polymers is larger than that of the extractable fractions. The unextractable polymer isolated from aerosil additionally possesses a strong UV absorption at 26,000 cm^{-1} if F^- or Cl^- are present as counterions. The qualitative results of the analysis of the unextractable fractions can be summarized briefly:

1. Initiation by means of triphenylmethylium bromide–aerosil principally yields an unextractable fraction with M_n = 4000 g/mol and a M_w/M_n ratio of 1.4.
2. Initiation by means of triphenylmethylium chloride–aerosil yields two unextractable fractions, the larger of which has M_n = 4000 g/mol and a smaller fraction between 300 and 500 g/mol.
3. Initiation by means of triphenylmethylium fluoride–aerosil also yields two fractions as in 2; the main fraction has an M_n between 300 and 500 g/mol (90%).
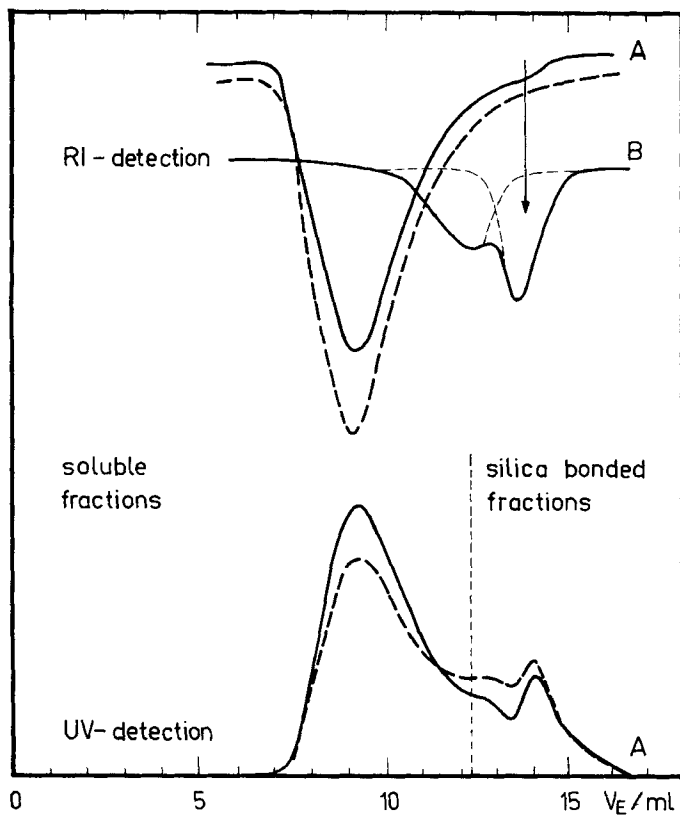
FIG. 2. GPC traces of the fractions obtained by means of KOH or HF treatment from the crude composite after polymerization by means of triphenyl-methylium chloride–aerosil initiation. A (---): Aerosil composite was treated with 40% HF. A (——): Aerosil composite was treated with 20% KOH. B (——): The crude aerosil obtained after filtering and drying was extracted with 1,2-dichloroethane before being treated with KOH (the RI detection shows the lower fraction at higher concentration).

The UV absorptions of the unextractable fractions on the aerosil surface indicate the presence of unsaturated bonds in conjugation with aromatic systems. These species are derived from diphenylpolyenes which are formed by proton abstraction from an allylic ion by basic species such as strong nucleophilic counterions, F^- or Cl^-, according to Plesch [33].

The formation of Si—O—C—bonds, poly-p-methoxystyryl ions and/ or unsaturated oligomers on the surface, and the mechanism of the reaction involved leading to the new solid composites will be discussed in another paper dealing with solid-state FTIR spectroscopy, solid-state ^{13}C-NMR spectroscopy, and other methods [30]. The cationic interfacial polymerization employed as a grafting technique onto silica may be suitable as a method for composite synthesis in comparison to established procedures [31, 32]. However, the present paper deals with the influence of the concentrations of the components, e.g., overall monomer and initiator concentrations, on the extractable, soluble polymer fractions.

Representative GPC plots, obtained by means of Method A, are shown in Fig. 3. Increasing the overall initiator concentration from 10^{-4} to 10^{-3} mol/L decreases the molecular weight. In the case of triphenylmethylium chloride-aerosil or fluoride-aerosil initiation, an additional lower molecular weight fraction gradually appears with increasing initiator concentration. The molecular weight of the smaller fraction is similar to the weight of the fractions remaining on the aerosil surface, but the extractable fractions do not contain double bonds as proved by ozonolysis experiments. The influences of the overall initiator concentration on the organic fractions interacting with the aerosil is shown in Fig. 4. The amount of polymer chemically bonded onto the surface is expressed by the % C analysis as AE-C (see Fig. 4).

It is obvious that interfacial polymerization does not occur below initiator concentrations which are required to yield aerosil composites as indicated in Fig. 4. However, the triphenylmethyl halide concentrations used without aerosil do not initiate the polymerization of p-methoxystyrene if water had been carefully excluded (see Experimental Section). Polymerization of p-methoxystyrene takes place in homogeneous systems of moderate polarity by means of triphenylmethyl halide initiation in the presence of acceptors or initiator concentrations above 5×10^{-3} mol/L as reported recently [17, 34]. With the latter conditions, a large number of simultaneous reactions take place and broad MWD curves have been found [17]. Advantageously, the extractable poly-p-methoxystyrene fractions obtained by means of interfacial polymerization possess
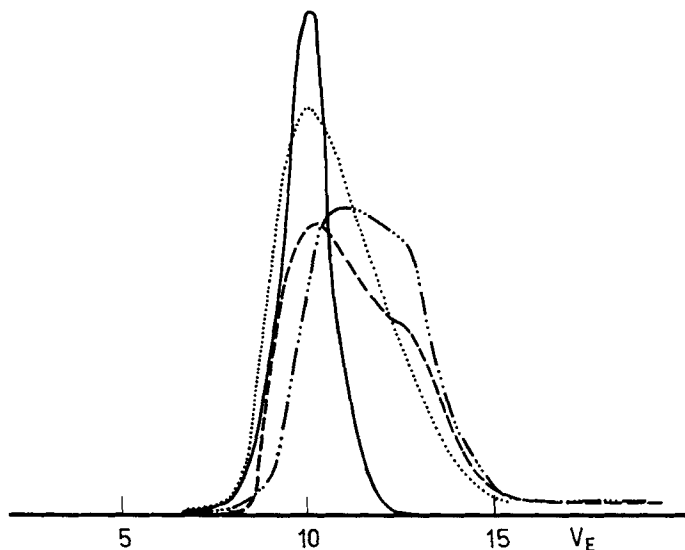
FIG. 3. Influence of the overall initiator concentration on the GPC traces of poly-*p*-methoxystyrene obtained by means of $(C_6H_5)_3C^+X^-$-aerosil initiation in 1,2-dichloroethane at 273 K. (——) X = Cl, 3 × 10^{-4} mol/L or X = F, 5 × 10^{-4} mol/L. (···) X = Br, 5 × 10^{-4} mol/L. (– –) X = Cl, 6 × 10^{-4} mol/L. (– ··· –) X = F, 1 × 10^{-3} mol/L.

a marrow MWD when low initiator concentrations are used, and initiation by means of triphenylmethylium bromide–aerosil yields polymers with unimodal distribution. We have applied the Sczwarz equation [35] (Eq. 7) for this initiating system, as seen in Fig. 5.

$$\overline{DP} = [M]/[R^+] \tag{7}$$

The linear relationship $\overline{DP}$ versus $1/[(C_6H_5)_3CBr]$ approaches living behavior, and transfer to the monomer is suppressed as seen from the M_w/M_n ratio when the initiator concentration used is below 5 × 10^{-5} mol/L. Increasing initiator concentrations lead to broader distributions and lower molecular weights of the extractable polymers.

Influence of the Monomer Concentration

Increasing monomer concentration leads to increasing amounts of unextractable polymer, as shown in Fig. 6.

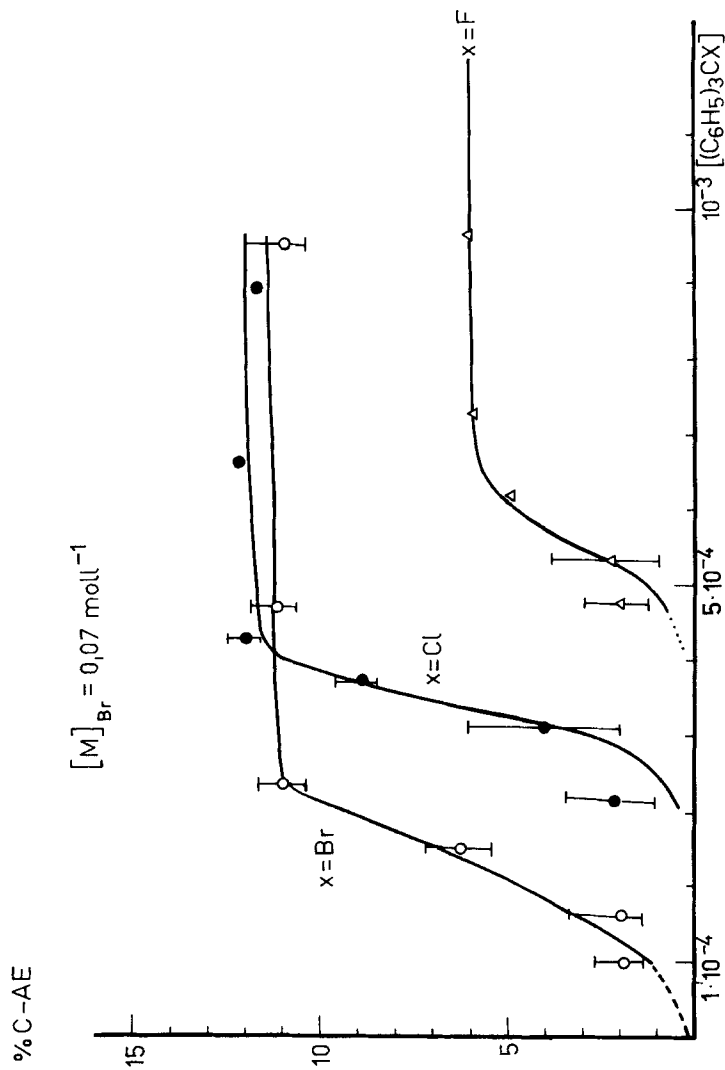A comparison of the two methods of interfacial polymerization shows

FIG. 4. Carbon content (AE-C) of the composite obtained as a function of the overall initiator concentration at 273 K.
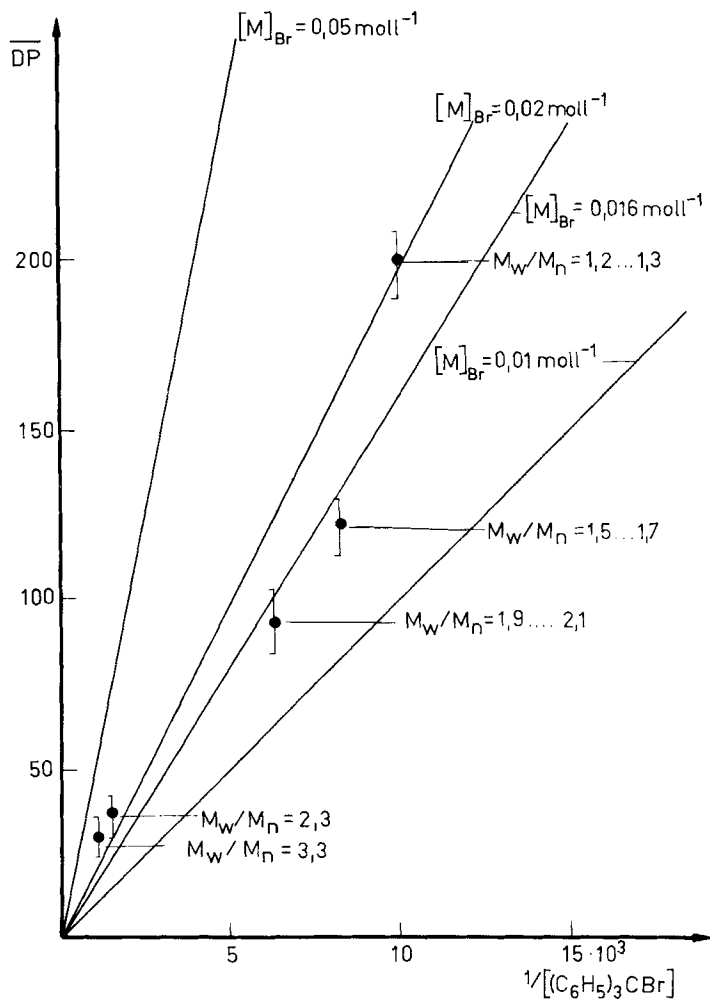
FIG. 5. Dependence of the *DP* and the M_w/M_n ratios of poly-*p*-methoxystyrene on the overall triphenylmethyl bromide concentration by means of $(C_6H_5)_3C^+Br^-$-aerosil initiation in 1,2-dichloroethane at 273 K. The solid lines are theoretical plots for assumed monomer concentrations according to Eq. (7).
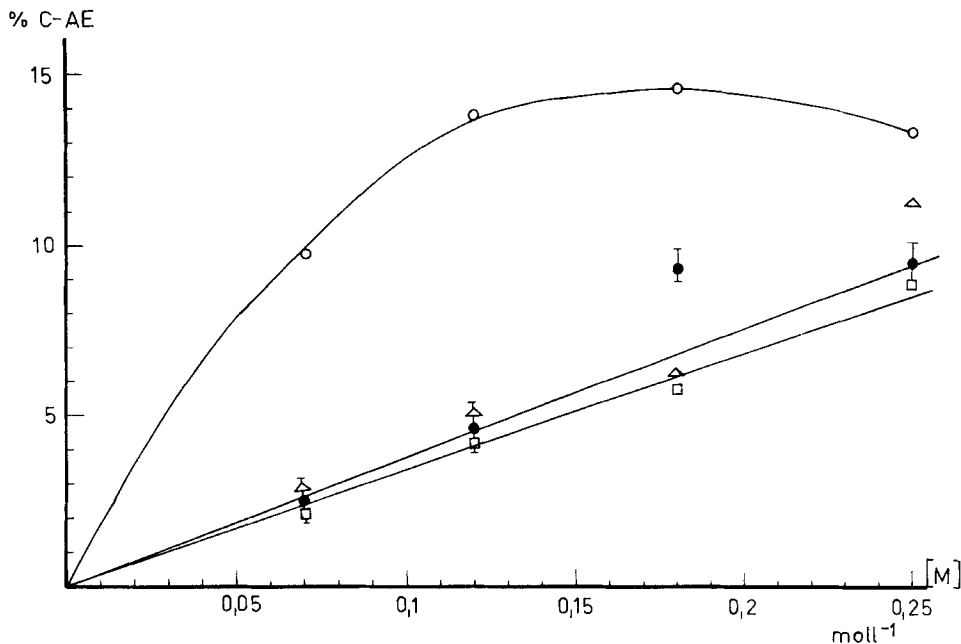
FIG. 6. Carbon content (AE-C) of the composite obtained as a function of the overall monomer concentration at 273 K. (○): Triphenylmethylium chloride–aerosil initiation (A). (●): Triphenylmethylium chloride–aerosil initiation (B). (□): Triphenylmethylium fluoride–aerosil initiation (A). (△): Triphenylmethylium bromide–aerosil initiation (A). The letters in parentheses indicate the experimental method used.

that Method A generates the composite while Method B mainly yields extractable polymers as shown for the initiation with triphenylmethylium chloride–aerosil (see Fig. 6). The composition of polymer included in the aerosil composite does not exceed 15% carbon. Thus, monomer concentrations higher than 0.25 M do not enhance composite synthesis, and monomer conversion is not complete above this concentration. Surprisingly, the extractable polymer fractions are independent of the overall monomer concentration when low initiator concentrations are used. The M_w/M_n ratios of the soluble polymer are narrow: $M_w/M_n = 1.2$ to 1.3. The GPC plots are shown in Fig. 7. These results suggest that the actual available monomer concentration is constant in relation to the effective initiator concentration. Therefore, we conclude that the propa-
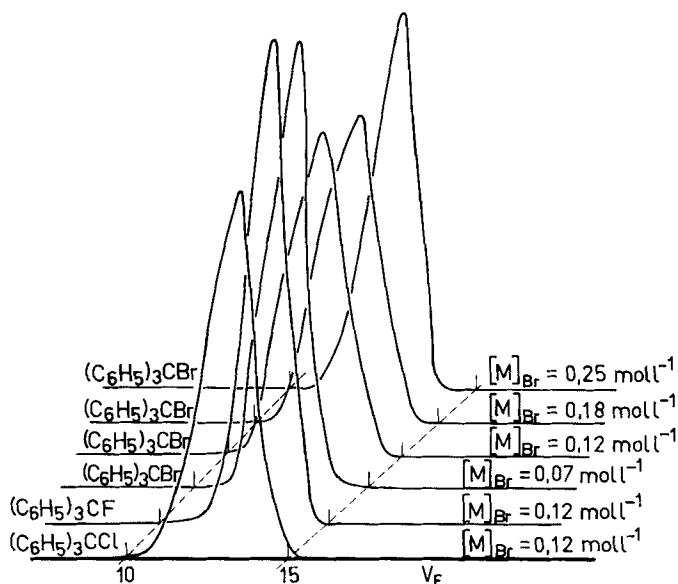
FIG. 7. Influence of the overall monomer concentration on the GPC traces (soluble part) of poly-p-methoxystryrene obtained by means of $(C_6H_5)_3C^+X^-$-aerosil initiation in 1,2-dichloroethane at 273 K (Method A). X = Br, 1×10^{-4} mol/L. X = Cl, 3×10^{-4} mol/L. X = F, 5×10^{-4} mol/L. The concentrations are given with respect to the bulk phase.

gation process is more rapid than the diffusion of monomer through the interface (compare Fig. 1). UV measurements support the argument that the concentrations of the carbenium ions, $(C_6H_5)_3C^+$, at the surface are equal for all initiators employed under these experimental conditions (Fig. 7) [20]. However, the actual behavior of charged molecules partitioning between solid–liquid interfaces is much more complicated and is affected by the formation of several ionic layers normally present in interfacial and ion-transfer phenomena (see Discussion Section).

DISCUSSION

During the cationic polymerization of p-methoxystyrene initiated by triphenylmethyl halides in solvents of moderate polarity, proton transfer from the chain end to nucleophilic counterions is an important reaction

which leads to polyhalides such as $X(HX)_n^-$ [17]. In the case of interfacial polymerization involving bromide counterions, transfer reactions are suppressed as indicated by linear plots of $\overline{DP}$ versus $1/(C_6H_5)_3CBr$ and the narrow MWD curves. This behavior suggests that a chain carrier involving mainly ion pairs and the corresponding counterion is "stabilized" by silanol groups which act as acceptors. In the case of triphenylmethylium fluoride- or chloride–aerosil initiation, proton transfer reactions are occurring, and HF_2^- or HCl_2^- may be present as counterion intermediates. However, the appearance of polymer fractions containing double bonds supports the assumption that proton transfer reactions do occur and counterion aggregation is taking place. The smaller mass fraction obtained from triphenylmethylium fluoride- or chloride–aerosil initiation possess intensive UV absorptions at 33,000 and 26,000 cm^{-1}. This indicates the formation of substituted butadiene units, similar to those obtained by Plesch [33] in the pseudocationic polymerization of styrene with $HClO_4$ in CH_2Cl_2, and suggests a similar termination mechanism. Exclusive interfacial polymerization is due to a balance in the two effects of the strong nucleophilicity of halides: the binding of the ionic chain carrier via silanol-anion coordination at the surface and the lowering of the potential energy of the active chain carrier.

We have recently emphasized that an effective interaction of the counterion with the propagating chain end is of key importance in the suppression of competing reactions deleterious to living polymers [8]. First attempts in the field of interfacial polymerization were carried out with HCl as an initiator in the presence of a variety of metal oxides as coinitiators in isobutylvinyl ether polymerization [36]. However, no detailed studies were reported and the actual behavior of ion pairs participating in propagating processes onto surface groups is not completely understood. The simple coordination point of view suggests the presence of a cationic interfacial species, but this is not sufficient to explain all experimental results, i.e., the ratio of both resulting composites and extractable polymers. According to the Stern model [37], the charges at the surface of the solid are compensated for by counterions forming two different layers. The layer close to the surface is immobile (Stern layer, SL) while the other one allows diffusion of ions due to thermal motion (diffuse layer, DL). The interface potential (Ψ_D) and interface charge density cannot be measured directly [38, 39]. However, the electrokinetic or zeta potential can be determined by electrokinetic measurements [39]. The zeta potential is defined as the potential of the slipping plane where
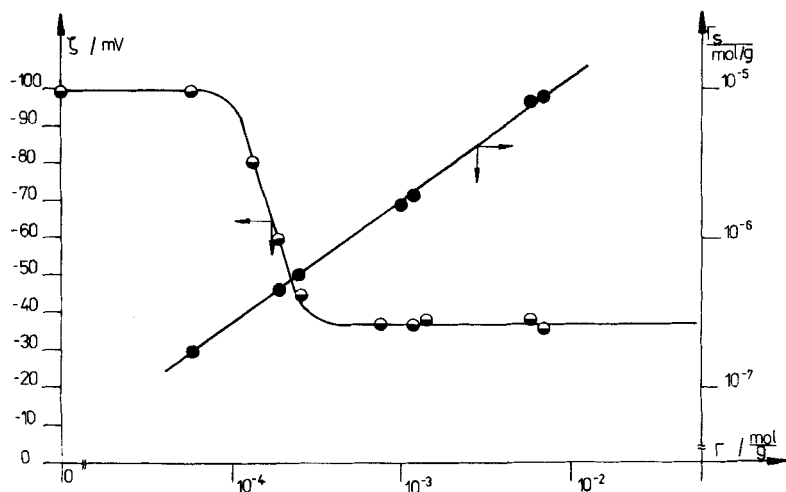
FIG. 8. Zeta potential (○) of aerosil adsorbates and Freundlich plots (●) as functions of the overall $(C_6H_5)_3CBr$ concentration in 1,2-dichloroethane at 293 K.

the ionic species are removed from the surface by electric forces (see Experimental Section). The formation of electrochemical double layers of silica in organic solvents may be due to a donor attack on the surface groups. A general theory for the electrokinetic potential in solvents of moderate polarity is not available as yet because the relationship of the Stern layer and "diffuse layer" is unknown [27]. Some of the detailed aspects of this subject are outlined in a paper with Jacobasch [23]. A comparison of the effect of both zeta potential and adsorption as a function of triphenylmethyl bromide concentration is shown in Fig. 8.

   The adsorption of triphenylmethyl halides onto aerosil leads to their ionization, and the adsorption process can be quantitatively described by the Freundlich isotherm [40]. Similar behavior has been found for a variety of triphenylmethyl derivatives [23]. The decrease of the negative zeta-potential values with increasing triphenylmethyl bromide concentrations in comparison to the value of the bare aerosil particle in 1,2-dichloroethane is caused by an increase of the Stern layer, which contains mainly triphenylmethylium halide ion pairs. The covering of the aerosil
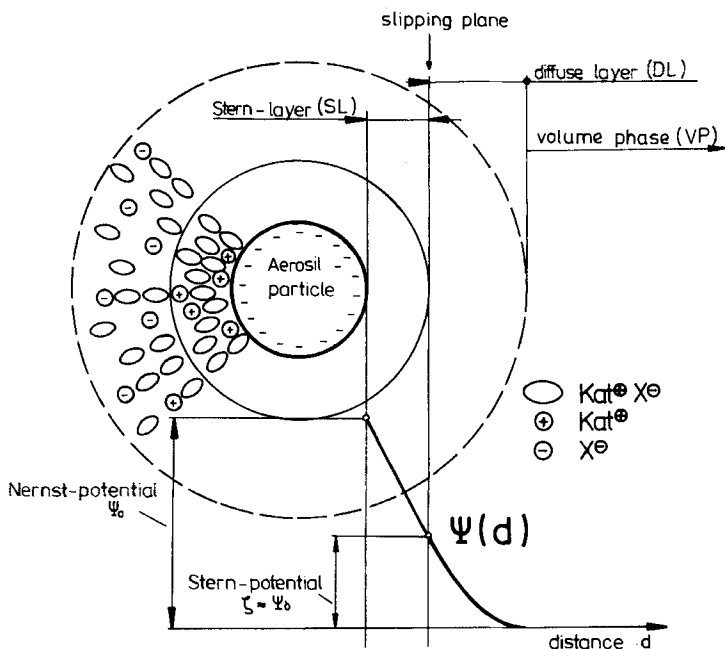
FIG. 9. Model for electrochemical multilayers of triphenylmethylium halides (or other ion pairs) spherically surrounding the aerosil in organic liquids.

forming the Stern layer is complete in the triphenylmethyl bromide concentration range of 5×10^{-4} mol/L. This means that the concentration of triphenylmethylium bromide ion pairs on the aerosil surface determining the Stern layer is in the range of 10^{-6} mol/g of the solid. Any further increase of the overall triphenylmethyl bromide concentration does not change the zeta potential. Therefore, we conclude that any further increase of triphenylmethyl bromide concentration (see the adsorption plots in Fig. 8) at the surface is due to an increase of ion pairs of the diffuse layer. These results agree with the model of Stern [37] which proposes multilayer formation (Fig. 9).

According to this model, three different reaction spheres have to be taken into account in triphenylmethyl halide initiation in conjunction with aerosil:

1. The Stern layer (SL).
2. The diffuse layer (DL); the thickness of this layer is much greater

than the diameter of the stock aerosil particle, and with the help of the method of Labib and Williams [27], the thickness of the diffuse layer has been estimated to be greater than 100 μm.

3. The volume (bulk) phase (VP).

Thus, the overall polymerization rate relating to monomer conversion is given by the fundamental equation

$$d[M]/dt = k_{SL}[M][R^+] + k_{DL}[M][R^+] + k_{VP}[M][R^+] \qquad (8)$$

In the case of $[(C_6H_5)_3CBr] \leq 5 \times 10^{-3}$ mol/L, the volume term can be neglected because $[R^+]_{VP} = 0$.

In comparison to the zeta-potential plots of the triphenylmethyl halide, the decrease of the zeta-potential values with increasing p-methoxystyrene concentration is not drastic. In the case of p-methoxystyrene adsorption, a Langmuir behavior was found, which usually indicates the formation of a monolayer equilibrium. Zeta-potential and adsorption plots are shown in Fig. 10.

A comparison of the zeta-potential plots from Figs. 9 and 10 shows that the relevant spheres for interfacial polymerization are mainly influ-
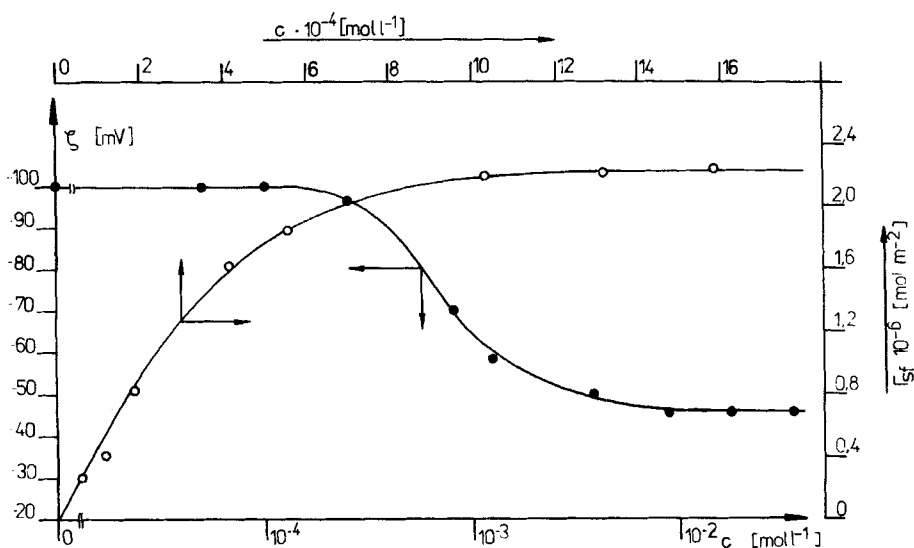

FIG. 10. Zeta potential (●) of aerosil and Langmuir plots (○) as functions of the overall p-methoxystyrene concentration in 1,2-dichloroethane at 293 K.

enced by the triphenylmethylium halide multilayers because of a stronger dipole–dipole interaction of ion pairs relative to the uncharged monomer. The additional formation of polymers during interfacial polymerization significantly increases the plane of shear [41].

A decrease of the zeta-potential value occurs in the same range of concentration as that of composite formation, as seen from a comparison of Figs. 4 and 8. This shows that the formation of the composites mainly occurs in the Stern layer. Taking into account the adsorption isotherm in Fig. 8, it is estimated that the lowest essential initiator concentration requires the participation of 2–3% of the silanol groups.

It is assumed that a dynamic equilibrium of triphenylmethylium halide–aerosil is operative between the Stern layer and the diffuse layer. Therefore "minute amounts" of carbocations must be present in the diffuse layer because extractable polymer is also obtained at very low initiator concentration [below 10^{-6} mol/g of $(C_6H_5)_3C^+X^-$ on aerosil]. These "minute amounts" of carbocations initiate the polymerization which proceeds in the diffuse layer, leading to soluble polymer with narrow MWD curves, and the actual concentration of monomer is larger than the concentration of the active chain carrier. Triphenylmethylium halide–aerosil initiation suggests that the "minute amounts" of cations operative during propagation do not lead to pseudocationic behavior as is the case for homogeneous systems where activated esters are dominant [6, 7]. This argument is supported by the independence of the MWD curves of the soluble polymers from the overall monomer concentration.

CONCLUSIONS

The results in this paper show that the polymerization of *p*-methoxystyrene initiated by triphenylmethylium halide–aerosil in 1,2-dichloroethane suspensions undergoes conversion into two products: polymers with a narrow MWD and composites. The controlled synthesis accounts for the "living" behavior of the interfacial species on the aerosil surface and between the interfacial layers. According to the model of Stern, the following rules are suggested:

> Composite synthesis takes place on the surface which is in contact with the Stern layer, and soluble polymer is formed in the diffuse layer of the solid–liquid interface.
>
> The balance between the Stern layer and diffuse layer, which depends on solvent, surface of the solid, size, initiator, monomer,

temperature, and other external influences, is the fundamental factor which determines the reaction products which are either composites or soluble polymer in heterogeneous catalysis.

These problems will be dealt with in forthcoming papers.

REFERENCES

[1] A. Gandini and P. H. Plesch, *J. Chem. Soc.*, p. 4826 (1965).

[2] P. H. Plesch, *Pure Appl. Chem., 12*, 117 (1966).

[3] J. P. Kennedy, *J. Macromol. Sci. — Chem., A18*, 1158 (1982/83).

[4] T. Higashimura and M. Sawamoto, *Adv. Polym. Sci., 62*, 49 (1984).

[5] G. Heublein and S. Spange, *Makromol. Chem., Makromol. Symp., 3*, 65 (1986).

[6] K. Matyjaszewski, *Ibid., 13/14*, 433 (1988).

[7] P. H. Plesch, *Ibid., 13/14*, 375 (1988).

[8] G. Heublein, S. Spange, and A. Ulbricht, *Ibid., 13/14*, 235 (1988).

[9] J. P. Kennedy, *Makromol. Chem., Suppl., 7*, 171 (1984).

[10] W. Obrecht and P. H. Plesch, *Makromol. Chem., 182*, 1459 (1984).

[11] S. Spange, Thesis B, Friedrich-Schiller University, Jena, 1988.

[12] P. H. Plesch, *The Chemistry of Cationic Polymerization*, Pergamon, New York, 1963, Chap. 1.

[13] S. Spange, G. Heublein, R. Dreier, and F. Taeger, *Acta Polym., 39*, 214 (1988).

[14] A. Gandini and P. H. Plesch, *Proc. Chem. Soc.*, p. 240 (1964).

[15] M. Bölke, S. Spange, P. Hallpap, R. Dreier, and G. Heublein, *Makromol. Chem., Rapid Commun., 8*, 507 (1987).

[16] F. L. Dickert and F. Fackler, *Angew. Chem., 94*, 303 (1982).

[17] S. Spange, R. Dreier, G. Opitz, and G. Heublein, *Acta Polym., 40*, 55 (1989).

[18] E. M. Arnett and K. F. Cassidy, *Rev. Chem. Intermed., 9*, 27 (1988).

[19] S. Spange, P. Hortschansky, A. Ulbricht, and G. Heublein, *Z. Chem., 27*, 207 (1987).

[20] S. Spange, A. Ulbricht, and G. Heublein, *J. Prakt. Chem., 330*, 235 (1988).

[21] L. M. Dorfmann, R. J. Sujdak, and R. L. Jones, *J. Am. Chem. Soc., 98*, 4875 (1976).

[22] A. Ledwith, *Makromol. Chem., 175*, 1117 (1974).
[23] F. Simon, S. Spange, G. Heublein, H. J. Jacobasch, and M. Börner, *J. Polym. Colloid Sci.*, In Press.
[24] R. Cotrel, G. Sauvet, J. P. Vairon, and P. Sigwalt, *Macromolecules, 9*, 931 (1976).
[25] *Organic Synthesis*, Vol. III, p. 273.
[26] D. C. Henry, *Proc. R. Soc. (London), Ser. A, 133*, 106 (1931).
[27] M. E. Labib and R. Williams, *J. Colloid Interface Sci., 97*, 356 (1984).
[28] P. H. Plesch, *Z. Elektrochem., 60*, 325 (1956), discussion part.
[29] P. H. Plesch, *The Chemistry of Cationic Polymerization*, Pergamon, New York, 1963, Chap. 4, p. 151.
[30] S. Spange, B. Heublein, G. Heublein, F. Simon, and H. Schütz, Unpublished.
[31] A. Munir and E. J. Goethals, *Makromol. Chem., Rapid Commun., 2*, 693 (1981).
[32] A Vidal, A. Guyot, and J. P. Kennedy, *Polym. Bull., 2*, 315 (1980).
[33] A. Gandini and P. H. Plesch, *Eur. Polym. J., 4*, 55 (1968).
[34] G. Heublein and S. Spange, *Acta Polym., 33*, 509 (1982).
[35] M. Sczwarz, *Nature, 178*, 1168 (1956).
[36] S. Aoki, H. Nakamura, and T. Otsu, *Makromol. Chem., 115*, 282 (1968).
[37] O. Stern, *Z. Elektrochem., 30*, 508 (1924).
[38] H. J. Jacobasch, *Angew. Makromol. Chem., 128*, 47 (1984).
[39] V. Ribitsch, Ch. Jorde, J. Schurz, and H. J. Jacobasch, *Prog. Colloid Polym. Sci., 77*, 49 (1988).
[40] H. Freundlich, *Colloid Capillary Chem., London*, p. 242 (1922).
[41] M. A. Cohen Stuart and J. Mulder, *Colloids Surf., 15*, 49 (1988).

OBITUARY: GÜNTHER HEUBLEIN
(December 11, 1933–July 17, 1989)

After a long, severe illness, Professor Günther Heublein died in July 1989. His colleagues and coworkers have immediately felt his absence.

G. Heublein was a dedicated chemist. After his studies at the Univer-

sity of Jena (1952–1958), he received a PhD in the stereochemistry of amino alcohols in 1961 as a coworker of G. Drefahl. His postdoctoral work involved lectures and research on the stereodynamics of electrophilic addition reactions. He became a Lecturer in Theoretical Organic Chemistry in 1967 and was appointed Full Professor of Organic Chemistry in 1968. Since 1972 he had been head of the subdepartment "Theory of Organic Reactions" of the Department of Chemistry of Friedrich-Schiller University. His 305 papers, 73 patents, and 4 books were the result of the intensity and dedication with which he approached his work.

He held the opinion that a scientist should direct his interests to up-to-date research problems. As a consequence of coming from Drefahl's school, he turned from stereochemistry of organic reactions to cationic polymerization and, finally, to heterogeneous polymer analogous reactions. He did not hesitate to work in new fields and to encourage his coworkers to direct their work in unaccustomed directions. His success showed that he was right; the results of his work made him and his subdepartment an appreciated partner in the international scientific world. This was especially true in the research field of cationic polymerization. As a consequence, he received extensive international recognition and obligations. He was appointed head of the GDR delegation in the "Ionic Polymerization" group of the academies of socialist countries and a member of the scientific committee of the "International Symposia on Cationic Polymerization." The 7th ISCP in Jena in the summer of 1985 was an overwhelming success because of his leadership. He was co-editor of *Advances in Polymer Science* and on the Editorial Board of the *Journal of Macromolecular Science – Chemistry*. He was an affiliated member of the Polymer Chemistry Division of ACS, beginning in 1977. He visited all of the important centers of polymer chemistry to give lectures and to take part in congresses. He was invited to several countries, e.g., Bulgaria, Poland, USSR, Czechoslovakia, France, USA, Great Britain, FRG, and Japan.

The results of the practical work of G. Heublein included the synthesis of special types of polyvinyl alcohols (with H. Meissner), the selective polymerization of C_4 hydrocarbon mixtures, and the synthesis of hydrocarbon resins (with H. Hartung and D. Stadermann). He also made important contributions to the development of cationic polymerization, particularly in the investigation of donor–acceptor steering (with S. Spange), the quantification of ionic polymerizations (with P. Hallpap and R. Wondraczek), and transfer suppressed cationic polymerization (with K. H. Gührs and S. Spange). A comprehensive view to the field of

ionic polymerization may be found in his book *Zum Ablauf ionischer Polymerisationsreaktionen* (Akademie-Verlag, Berlin, 1975).

G. Heublein believed it was important to generalize experimental and theoretical results for steering reactions into practical, relevant systems. As a result, much practical chemistry came from his subdepartment, as demonstrated by the large number of patents issued from it.

The search for generalization determined the focus and activities of G. Heublein as a teacher. He conceived of and lectured on the subject "Reaction Theory," an integrative field he fought for and wrote about in his textbook *Einführung in die Reaktionstheorie* (Dtsch. Verlag Grundstoffind., Leipzig, 1984; with P. Hallpap and others). He was a dedicated teacher who sought direct contact with his students.

G. Heublein was aware that the responsibility of a scientist and professor goes far beyond the task of teaching and research. As a result, during his tenure as the Head of the Department of Chemistry (1977–1981), he developed the idea for a technical laboratory. He was head of the Division of Macromolecular Chemistry of the Chemical Society of the GDR for several years. He was awarded the National Prize for Science and Technology of the GDR for his important scientific work in 1984.

His colleagues and coworkers will not forget him—the creative and purposeful scientist, the successful academic teacher, and the thoughtful and friendly man Günther Heublein.