Methyl Methacrylate (MMA)–Glycidyl Methacrylate (GMA) Copolymers. A Novel Method to Introduce Sulfonic Acid Groups on the Polymeric Chains

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ABSTRACT: A new method has been described to introduce sulfonic groups in methyl methacrylate (MMA)–glycidyl methacrylate (GMA) copolymer. The polymer particles are suspended in water and reacted with sodium sulfite at 80 ± 1 °C in the presence of a cationic surfactant such as tetra-*n*-butylammonium bisulfate (TBABS) under nitrogen. Based on the data, it has been assumed that the cationic surfactants are adsorbed by a Langmuir type isotherm on the surface of the suspended MMA–GMA copolymer powder. The resulting positive charge would attract the nucleophilic sulfite ion. The reaction has been found to be first-order with respect to the epoxy group concentration in the copolymer (rate constant = 2.7×10^{-5} s^{-1} at 80 ± 1 °C). The addition of sulfite ions to the epoxy groups in the copolymer results in primary sulfonic acid and secondary hydroxyl groups as concluded from a strong ir absorption band at 1040 cm^{-1} (due to S=O stretching) and an NMR peak at δ 5.1 ppm (due to secondary hydroxyl hydrogen). The reaction rate varies with the nature of the counterion of the quarternary ammonium salt in the order $Br^- > HSO_4^- > Cl^-$. The conversion of the epoxy groups in the sulfite reaction increases with increasing concentration of sodium sulfite, with the presence of a solvent such as chloroform, and with increasing number average molecular weights ($\bar{M}_n$) of the MMA–GMA copolymer.

Polymers containing sulfonic acid groups in the form of free acid or salt have been studied intensively and many methods of synthesis have been described.[1–20] Two methods have generally been used for the preparation of such polymers: polymerization of sulfonated monomers, e.g., ethylenesulfonic acid or sodium vinyl sulfonate; and introduction of sulfonic acid groups in an existing polymer. Recently a comprehensive review paper has been published by Goethals,[21] summarizing the known methods for the preparation of polymers containing sulfonic acid groups.

The main problem associated with the direct polymerization method is that only small amounts of water-insoluble monomers, e.g., acrylonitrile, methyl acrylate, methyl methacrylate, and vinyl acetate, can be copolymerized with sodium ethylene sulfonate (SES) in aqueous media. However, copolymers of SES with vinyl acetate and with styrene are readily prepared in aqueous dimethyl sulfoxide.[22] Furthermore, concentration of the monomers is the controlling factor in this polymerization; both reaction rates and resulting molecular weights vary directly with monomer concentration. These findings are attributed to partial neutralization of the negative charges on the growing polymer chain, which in more dilute solutions would tend to repel the approach of monomeric ethylene sulfonate ions.[3] For this reason the method of introducing the sulfonic acid groups in an existing polymer by means of concentrated sulfuric acid, chlorosulfonic acid, or sulfur trioxide as such or in the form of a complex has become the most important method for controlled introduction of sulfonic acid groups. Of all polymers, polystyrene is the most widely used substrate for sulfonation. Several methods have been reported to prepare water-soluble or water-insoluble polystyrene sulfonates.[11–20]

The present paper reports a new method for introducing sulfonic acid groups in methyl methacrylate (MMA) polymer chains containing epoxy groups. The work is based on the studies of Schenck et al.,[23] that sparingly soluble epoxy compounds react with sulfite ions in aqueous solution to form sulfonic acid or salt derivatives. Copolymers of MMA with epoxy group containing monomer such as glycidyl methacrylate (GMA) suspended in water were treated with sodium sulfite at different concentrations and at different temperatures. No reaction was observed. This can be attributed to the higher affinity of the sulfite groups to water than to the hydrophobic polymer chains suspended in water. The phase separation prevents the sulfite groups to come in close contact with epoxy groups in the polymers, necessary for the reaction. Using the recently developed "phase transfer" catalysts,[24,25] where an ionic surfactant carries an ionic reagent from the aqueous phase to the organic phase, sulfonation of the epoxy groups in the polymer chains has been made possible. The use of cationic surface active agents as "phase transfer" catalyst has been reported earlier by Takeishi et al.[26] for the nucleophilic substitution of azide groups to poly(vinyl chloride) (PVC) chains in water suspension.

Polymers containing sulfonic acid groups find application as aqueous thickeners, impregnants, adhesives, and textile sizes. Because they are polyelectrolytes, they also have potential application in soil conditioning. They have also been found to be useful as ion exchange resins and as polymeric catalysts due to the activity of the strongly acidic sulfonic acid group.

Experimental Section

Materials. Copolymers of MMA and GMA ($\bar{M}_n$ = 5500) containing 34.0 mol % of GMA were synthesized by radical polymerization with 2,2′-azobis(isobutyronitrile) (AIBN) as initiator and thiophenol (TP) as chain transfer agent at 60 °C in vacuum-sealed ampoules, as previously described.[27] The MMA–GMA copolymers have been characterized by an ir method (28).

Quarternary ammonium salts were kindly supplied by Astra Meditec (Sweden) and were used without further purification.

Reaction of the Epoxy Groups in MMA–GMA Copolymers with Sulfite Ions in the Presence of Phase Transfer Catalysts. Tetra-*n*-butylammonium bisulfate (1.356 g; 0.4 mol/l.) (TBABS) as cationic surfactant and 2.52 g (1 mol/l.) of sodium sulfite were dissolved in 10 ml of distilled water, and 0.5 g of MMA–GMA copolymer containing 34.0 mol % GMA was added. The mixtures were sealed in ampoules after evacuating and filling them with nitrogen to avoid oxidation of the sulfite solution.[29] The reaction was carried out by tumbling the ampoules in an oil bath maintained at 80 ± 1 °C. The progress of the reaction was followed by ir and sulfur analysis of the isolated dried polymers.

Sulfur Content. Sulfur contents in the modified copolymers were determined in duplicate by the method described by Lysyj et al.[30] and an average value was taken. A 6% hydrogen peroxide solution was used and the sample (about 0.03 g) containing 5 to 10 mg of sulfur was accurately weighed in a gelatin capsule. A blank determination on the gelatin capsule was run, by merely omitting the sample. Small capsules obtained from a local drug store required a blank of 4.0 ml of 0.02 N NaOH solution.

$$\%S = \frac{\text{ml of NaOH} \times \text{N} \times 16.03}{\text{wt of sample} \times 10}$$

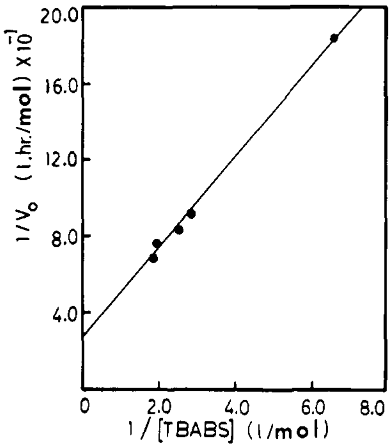


Figure 1. Plots of the reciprocals of reaction velocity (V_0) of the epoxy groups in MMA–GMA copolymers with $Na_2SO_3 \cdot 7H_2O$ vs. the reciprocals of concentration of the phase transfer catalyst (TBABS).

Results and Discussions

It has been shown earlier by Takeishi et al.[26] that the catalytic effects of tetra-*n*-butylammonium salts are stronger than those of other cationic surfactants. Therefore, tetra-*n*-butylammonium bisulfate (TBABS) was used. The initial rates of sulfonation are calculated from the amounts of the reacted sites in unit volume from estimations of percent sulfur content in the modified polymers.

The dependence of the reaction rate of the epoxy groups in the MMA–GMA copolymers with sodium sulfite as a function of TBABS concentration was studied. It was found that the rate increases with increasing ammonium salt concentration, but a saturation phenomenon was observed at high TBABS concentrations. This suggests that the cationic surfactant is adsorbed on the polymer surface by hydrophobic bonds. Then the positive charge attracts the sulfite ions to let them react with epoxy groups in the polymer chains. If this is so, the initial rate should be directly proportional to the amount of adsorbed TBABS,[31] i.e.,

$$V_0 = c[\text{TBABS}]_a \tag{1}$$

According to the Langmuir adsorption isotherm the amount of adsorbed TBABS will be (cf. ref 26):

$$[\text{TBABS}]_a = \frac{Ka[\text{TBABS}]_{eq}}{1 + K[\text{TBABS}]_{eq}} \tag{2}$$

Where K is the adsorption coefficient, a is the maximum amount adsorbed, and c is a rate constant which includes two concentration terms (copolymer and sodium sulfite) and the rate constant itself. Since the amount of TBABS adsorbed is small as compared to the added TBABS, the equilibrium concentration, $[\text{TBABS}]_{eq}$, in the aqueous phase is approximately equal to its initial concentration, $[\text{TBABS}]_0$. Thus from eq 1 and 2 one gets

$$V_0 = \frac{cKa[\text{TBABS}]_0}{1 + K[[\text{TBABS}]_0}$$

or

$$\frac{1}{V_0} = \frac{1}{cKa}\frac{1}{[\text{TBABS}]_0} + \frac{1}{ca} \tag{3}$$

To find evidence for the proposed mechanism, reciprocals of rates (V_0) vs. TBABS concentrations are plotted in Figure 1. The good linear relationship suggests that the reaction proceeds as proposed.

Table I
Kinetic Data for the Reaction of the Epoxy Groups in MMA–GMA Copolymers with Sodium Sulfite[a]

Reaction time, h	Av % S in polymers	Residual epoxy group concn in copolymer ($a_0 - x$), mol/l.	ln [$a_0/(a_0 - x)$]	$k \times 10^4$, s^{-1}
2	1.88	0.1193	0.22	0.30
3	2.73	0.1060	0.34	0.31
4	3.07	0.1007	0.39	0.27
5	3.80	0.0893	0.51	0.28
6	4.36	0.0805	0.61	0.28

[a] Initial epoxy group concentration (a_0) = 0.1487 mol/l.

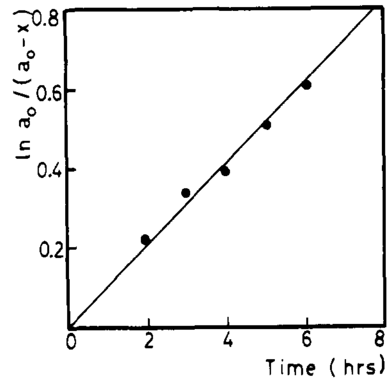


Figure 2. Kinetic plot of ln [$a_0/(a_0 - x)$] vs. reaction time.

To find further evidence for the reaction mechanism, both MMA–GMA copolymer and poly(methyl methacrylate) (PMMA) were treated with sodium sulfite in the presence of TBABS. Ir spectra of the washed and dried polymers were recorded as described earlier.[28] The presence of an adsorption band at 1040 cm^{-1} assigned to S=O stretching in the sulfite treated MMA–GMA copolymers and the absence of this band in sulfite treated PMMA further indicates that the epoxy groups in the copolymer are reacting with sodium sulfite.

This interpretation has further been confirmed by sulfur analysis. The extent of the reaction with sulfite could not be determined quantitatively from the appearance of the absorption band at 1040 cm^{-1} (due to S=O groups) and disappearance of the absorption band at 907 cm^{-1} (due to epoxy groups) as described earlier[28] because of changes in the absorptivity of the polymers with varying extent of the conversion of the epoxy groups.

From the data of the conversion vs. reaction time, kinetic data have been calculated and presented in Table I. A plot of ln [$a_0/(a_0 - x)$] vs. reaction time has been shown in Figure 2, where a_0 is the initial epoxy group concentration in the copolymer and x is the extent of epoxy group conversion derived from sulfur analysis.

The plot shows a straight line indicating a first-order reaction. Since the concentration of sulfite ions at the polymer surface is assumed to be constant and related to the concentration of TBABS, it is concluded that the rate of addition is proportional to the concentration of epoxy groups in the MMA–GMA copolymer. The average first-order reaction rate constant has been calculated to be 2.7×10^{-5} s^{-1} at 80 ± 1 °C.

The attack of the sulfite group is expected to be on the terminal carbon atom of the epoxy group from steric considerations. This assumption is supported by NMR spectra of the modified copolymer in deuterated DMSO at 60 MHz

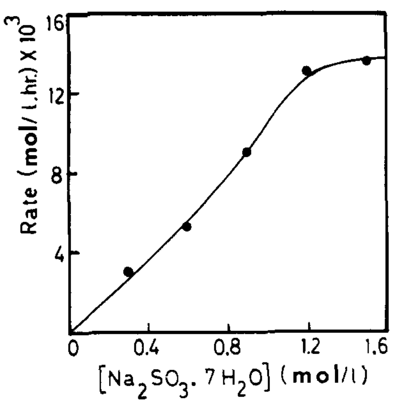


Figure 3. Dependence of the reaction rate of sulfonation with Na_2SO_3 of epoxy groups in MMA-GMA copolymer on the concentration of $Na_2SO_3 \cdot 7H_2O$.

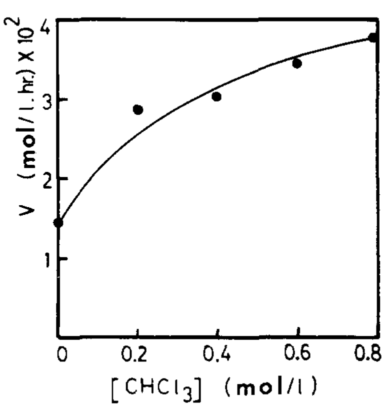


Figure 4. Influence of the addition of chloroform on the reaction rate (V) of sulfonation with Na_2SO_3 of epoxy groups in MMA-GMA copolymer.

Table II

Counterion Influence of the Phase Transfer Catalyst on the Reaction Velocity of the Epoxy Groups in MMA-GMA Copolymers with Na_2SO_3[a]

Catalyst	Reaction velocity, mol/(l. h)
Tetra-*n*-butylammonium bisulfate (HSO_4^-)	0.0131
Tetra-*n*-butylammonium bromide (Br^-)	0.0214
Tetra-*n*-butylammonium chloride (Cl^-)	0.0075

[a] Reaction conditions: 0.5 g of copolymer suspended in 10 ml of distilled water containing 2.52 g of Na_2SO_3 and 0.4 mol/l. of surfactant at 80 ± 1 °C.

Table III

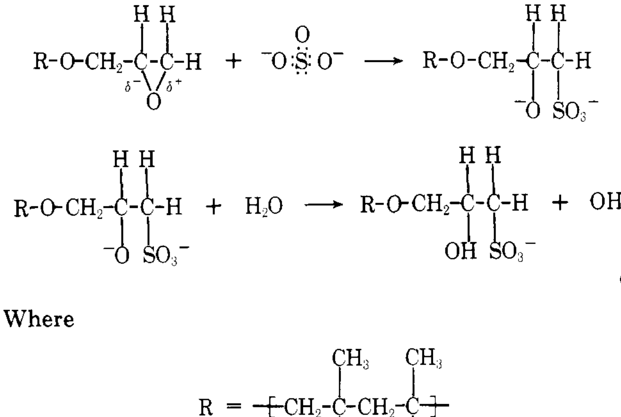
Dependence of the Percent Conversion of the Epoxy Groups in MMA-GMA Copolymers (GMA = 20 mol %) on Reaction with Na_2SO_3 vs. the Number Average Molecular Weight ($\bar{M}_n$) of the Copolymers[a]

No. av mol wt ($\bar{M}_n$)	Av %S in the sulfonated copolymer	% conversion of epoxy groups in sulfonated copolymer
5 000	0.94	16.2
8 000	1.88	32.4
35 200	2.12	36.5

[a] Reaction conditions: 0.5 g of copolymer suspended in 10 ml of distilled water containing 2.52 g of Na_2SO_3 and 1.356 g of TBABS at 80 ± 1 °C.

giving a peak with the chemical shift δ 5.1 ppm, which is normal for secondary hydroxyl protons.

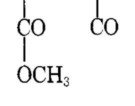
The reaction mechanism can schematically be represented as follows:



(i)

(ii)

Where



$$R = -[CH_2-\underset{\underset{\underset{OCH_3}{|}}{CO}}{\overset{CH_3}{C}}-CH_2-\underset{CO}{\overset{CH_3}{C}}]-$$

This reaction scheme is also supported by the fact that no reaction was found with sodium bisulfite alone. The failure of a bisulfite ion attack on the epoxy group was also shown earlier[23] and explained as due to the asymmetric structure of the bisulfite ion. The reaction conditions have been studied further. The influence of sodium sulfite concentration at constant concentration of cationic surfactant ([TBABS] = 0.35 mol/l.) and the influence of an added solvent such as chloroform are shown in Figures 3 and 4.

The increase in the reaction rate with increasing sodium sulfite concentration can be attributed to the salting out effect at higher salt concentrations as shown earlier.[32] The detailed kinetics would be more complicated because both the equilibrium constant of ion dissociation of the quarternary salt and the salting out effect of sodium sulfite seem to influence the reaction rate.

The counterion influence of the quarternary ammonium salts on the reaction rate of the epoxy groups with sodium sulfite has been studied and the data are presented in Table II.

It is evident that the reaction rate varies with the counterion in the order $Br^- > HSO_4^- > Cl^-$. This can be attributed to solubility and ionic character of the counterion which varies in the reverse order, i.e., $Cl^- > HSO_4^- > Br^-$.

The dependence of the extent of epoxy group conversion on the number average molecular weights ($\bar{M}_n$) has been presented in Table III. It is evident from the results that the percent conversion increases with increasing $\bar{M}_n$. It has been shown earlier[11,16] that during the sulfonation of polystyrene, sulfone cross-links were formed which affected the solubility of the polymers and also increased the solution viscosity after modification. In order to study a similar behavior in this case the relative viscosities of 0.1, 0.2, 0.3, and 0.4% solutions of MMA-GMA copolymer ($\bar{M}_n$ = 35 200, GMA = 20 mol %) initially and after modification with sodium sulfite (% conversion = 36.5%) were determined in chloroform and DMSO respectively at 30 ± 1 and 50 ± 1 °C with an Ubbelohde viscometer.

A slight increase in relative viscosity has been observed after modification which cannot, however, be attributed with certainity to cross-linking during the modification reaction, because viscosity of a polymer in solution is strongly dependent on the nature of the solvent. Further measurements are needed to establish the influence, if any, on the molecular weight of the sulfonation reaction. The solubility test showed that the modified copolymers are insoluble in chloroform but soluble in DMSO. The copolymers containing higher content of sulfonic groups are soluble in water also.

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References and Notes

(1) D. S. Breslow and G. E. Hulse, *J. Am. Chem. Soc.*, **76**, 6399 (1954).
(2) W. Kern and R. C. Schulz, *Angew. Chem.*, **69**, 153 (1967).
(3) D. S. Breslow and A. Kutner, *J. Polym. Sci.*, **27**, 295 (1958).
(4) A. Kutner and D. S. Breslow, "Encyclopedia of Polymer Science and Technology," Vol. 6, Interscience, New York, N.Y., 1967, p 455.
(5) R. L. Baechtold (American Cyanamid Co.) U.S. Patent 3,203,938 (1965).
(6) R. H. Wiley, *J. Polym. Sci.*, **28**, 163 (1958).
(7) R. H. Wiley, N. R. Smith, and C. C. Ketteren, *J. Am. Chem. Soc.*, **76**, 720 (1954).
(8) R. H. Wiley and S. F. Reed, *J. Am. Chem. Soc.*, **78**, 2171 (1956).
(9) A. O. Jakubovic, *Chem. Prod. Chem. News*, **23**, 257 (1960).
(10) K. A. Kun, *J. Polym. Sci., Part A-1*, **4**, 847 (1966).
(11) H. H. Roth, *Ind. Eng. Chem.*, **49**, 1820 (1957).
(12) D. C. Ingles, *Aust. J. Chem.*, **12**, 97 (1959).
(13) British Patent 829,704 (1960).
(14) M. Kato, T. Nakagawa, and H. Akamatsu, *Bull. Soc. Chim., Jpn.*, **33**, 322 (1960).
(15) W. R. Carrol and H. Eisenberg, *J. Polym. Sci., Part A-2*, **4**, 599 (1966).
(16) H. H. Roth, *Ind. Eng. Chem.*, **46**, 2435 (1954).
(17) R. Signer, A. Demagistri, and C. Müller, *Makromol. Chem.*, 18/19, 139 (1956).
(18) G. L. Starobinets, L. T. Sevast'yanova, and G. L. Bulatskaya, *Zh. Prikl. Khim. (Leningrad)*, **33**, 107 (1960).
(19) G. F. d'Alelio (Koppers Co.) U.S. Patent 2,631,127 (1953).
(20) D. W. Fox and P. Skenian (General Electric Co.) U.S. Patent 3,259,592 (1966).
(21) E. J. Goethals, "Reactions on Polymers," J. A. Moore, Ed., D. Riedel Publishing Co., Proceedings of the NATO Advanced Study Institute, July 15–25, 1973, p 320.
(22) W. Kern, V. V. Kali, and B. Scherhag, *Makromol. Chem.*, **32**, 37 (1959).
(23) R. T. E. Schenck and S. Kaizerman, *J. Am. Chem. Soc.*, **75**, 1636 (1953).
(24) A. Brändström and L. Junggren, *Acta. Chem. Scand.*, **23**, 2204 (1969).
(25) C. M. Starks, *J. Am. Chem. Soc.*, **93**, 195 (1971).
(26) M. Takeishi, Y. Naito, and M. Okawara, *Angew. Makromol. Chem.*, **28**, 111 (1973).
(27) S. Paul and B. Rånby, *J. Polym. Sci. Polym. Chem. Ed.*, in press.
(28) S. Paul and B. Rånby, *Anal. Chem.*, **47**, 1428 (1975).
(29) H. N. Terem and A. H. Isnel, *Istanbul Univ. Fen. Fak. Mecm., Seri. A*, **17**, 138–152 (1952).
(30) I. Lysyj and J. E. Zarembo, *Anal. Chem.*, **30**, 428 (1958).
(31) S. Glasstone, "The Elements of Physical Chemistry," Van Nostrand, New York, N.Y., 1946, p 548.
(32) W. K. Mathew, J. W. Larson, and M. J. Pikal, *Tetrahedron Lett.*, 513 (1972).

Inverse Gas Chromatography in the Vicinity of T_g. Effects of the Probe Molecule

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ABSTRACT: The chromatographic behavior of polymer stationary phases in the vicinity of their glass transition temperature is discussed in terms of column parameters and magnitude of probe interactions with the stationary phase. Past failures of the method to detect a known transition of the polymer are critically examined and accounted for. It is shown that solubility of the probe in the polymer, while an important factor, is not sufficient to characterize the polymer-probe system near T_g. Interactions of the probe with both bulk and surface of the stationary phase must be considered in such studies. The relationship between the chromatographic behavior near T_g and the limiting value of the surface tension of the polymer-probe solution is established.

The generality of the detection of the glass transition temperature (T_g) of polymer stationary phases by inverse gas chomatography seems at present well established. Since the first communication of Smidsrφd and Guillet[1] reporting a reversal from the normal chromatographic variation at T_g, a large variety of polymeric materials has been successfully investigated.[2-5] The glass transition temperatures so derived were in excellent agreement with results from other techniques.

During the same period, however, several studies revealed that, inexplicably, linear retention diagrams could be recorded through the T_g of the stationary phase.[6-8] Moreover, the requirement put forward by Smidsrφd and Guillet,[1] that the probe must be a nonsolvent of the polymer investigated, has proven invalid in some instances.[7,8] As a result, the ability of the gas chromatographic (GC) technique to provide conclusive evidence as to the existence of a transition in a polymer stationary phase could be severely limited.

It is the purpose of this communication to investigate the reasons which have led to past failures and to assess the importance of the nature of the probe molecule in the detection of the glass transition temperature by inverse gas chromatography.

Experimental Section

Experimental procedure, instrumentation, and polymers were identical with those described in earlier publications.[4,9] The solid (mp 164 °C) perfluoro *n*-eicosane, kindly donated by R. H. Dettre (E. I. Du Pont de Nemours and Co.), was injected into the carrier gas stream with a solid sampler. Table I summarizes the column parameters of the present work.

Vapor pressures of probe molecules required to compute activity coefficients were taken from standard literature sources.[10]

Bulk and surface retention volumes needed to calculate limiting values of the solution surface tension, $(\partial\gamma/\partial w_1)^\infty$, were obtained from published retention diagrams. Their values at T_g were determined by extrapolation of the linear portions of the retention diagrams above and below T_g, for equilibrium bulk sorption and surface adsorption, respectively. In the latter case the surface retention volumes, denoted U_s, were expressed in cm^3 m^{-2}. The surface area of the stationary phase required to compute U_s was obtained from the accessible surface area of the inert support as determined in an earlier publication.[9]