BRNO UNIVERSITY OF TECHNOLOGY
Faculty of Chemistry
Chemistry of Materials

Mgr. František Kučera

HOMOGENEOUS AND HETEROGENEOUS SULFONATION OF POLYSTYRENE

HOMOGENNÍ A HETEROGENNÍ SULFONACE POLYSTYRENU

SHORT VERSION OF PHD THESIS

Branch:	Macromolecular Chemistry
Supervisor:	Prof. RNDr. Josef Jančář, CSc.
Opponents:	Doc. RNDr. Jaroslav Petrůj, CSc. Prof. Ing. Petr Sáha, CSc. Prof. Robert A. Weiss

Date of PhD Thesis Defense: September 9, 2001

KEY WORDS

Polystyrene, Sulfonation, Ionomers

KLÍČOVÁ SLOVA

polystyren, sulfonace, ionoměry

MÍSTO ULOŽENÍ CELÉ PRÁCE

areálová knihovna FCH VUT v Brně, Purkyňova 118, Brno 612 00

ISBN 80-214-2022-7
ISSN 1213-4198

TABLE OF CONTENTS

1 ACTUAL KNOWLEDGE OF SULFONATION REACTION

1.1 Sulfonation reaction

Sulfonation is an electrophilic substitution reaction used to attach the sulfonic group (~SO_3H) on a molecule of an organic compound (Equation 1.1). Sulfonating agents may be defined as compounds that are able to replace carbon-bonded hydrogen in a substrate molecule by ~SO_3H group.

$$RH + SO_3 \longrightarrow R\text{-}SO_3H \tag{1.1}$$

The basic sulfonating agent is sulfur trioxide (SO_3) [1–5] and its derivatives such as sulfuric acid (H_2SO_4), oleum, chlorosulfonic acid (HSO_3Cl), acyl sulfates and addition compounds of sulfur trioxide (complexes). The major advantages for SO_3 appear to be rapid and complete reactions, no external energy requirement to complete sulfonation reaction.

The release of the ~SO_3H group was the reverse process to sulfonation, commonly described as desulfonation (or hydrolysis of ~SO_3H group) [6–8]. The ~SO_3H groups can be removed from sulfonated compounds with dilute solutions of acids or with water (Equation 1.2).

$$R\text{-}SO_3H + H_2O \longrightarrow RH + H_2SO_4 \tag{1.2}$$

Due to the presence of relatively highly reactive ~SO_3H groups, a crosslinking reaction between the molecules of the sulfonated product can occur adding more complexity to the assumed reaction scheme (Equation 1.3). Very little information on the crosslinking mechanism has been found in literature [9], however, it was established that crosslinking reaction rate increased with increase of reaction temperature. Crosslinked sulfones are very stable compounds, their decomposition can be achieved only by melting with alkaline hydroxides as shown in Equation 1.4.

$$2R\text{-}SO_3H \longrightarrow R\text{-}SO_2\text{-}R + H_2SO_4 \tag{1.3}$$

$$R\text{-}SO_2\text{-}R + NaOH \xrightarrow{\Delta T} R\text{-}SO_3Na + RH \qquad R = \text{aromatic ring} \tag{1.4}$$

The sulfone yield was dependent on the reaction temperature. Yield of about 30 % of the sulfone was observed for reactions at a temperature range from 70°C to 80°C and about 50% of the sulfone arised when reaction was carried out within the interval from 150°C to 200°C. The sulfone yield was reduced by the sulfonation with liquid SO_3 at about −10°C, or by addition of the acetic acid.

1.2 Mechanism of benzene sulfonation using SO_3

General sulfonation reaction scheme showed in Figure 1.1. is assumed [10, 11] to describe the mechanism of electrophilic sulfonation reaction on the aromatic ring satisfactorily. In agreement with the proposed scheme and results of kinetic studies [12–14], both reacting molecules determine the rate of sulfonation and this electrophilic substitution can be considered a bimolecular reaction of the second order (S_E2 mechanism):

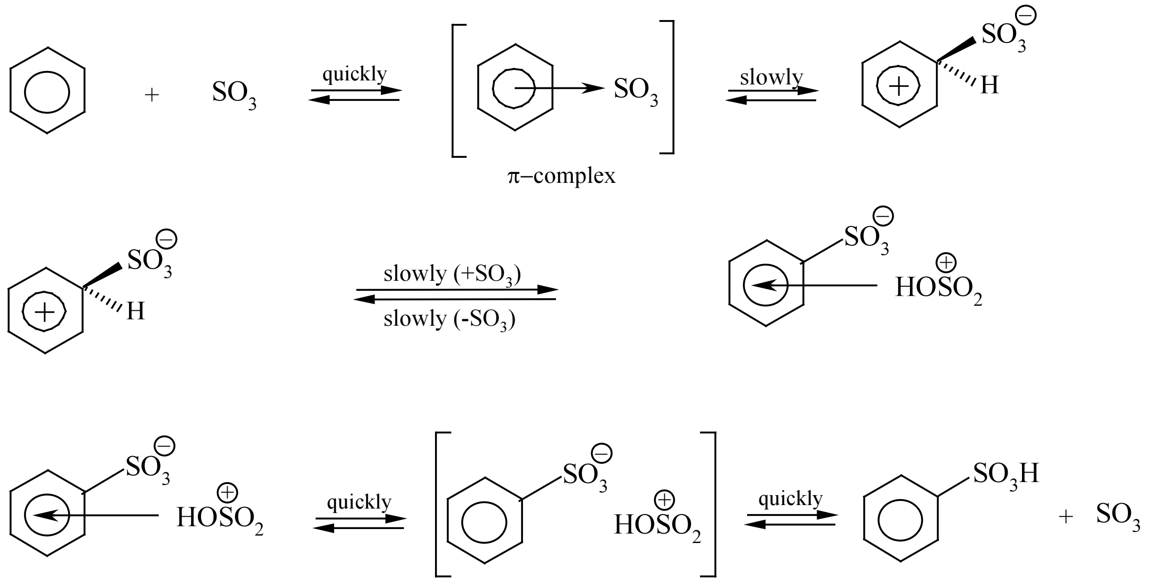


Figure 1.1 *Mechanism of the benzene sulfonation using SO_3 [46]*

The substituent attached on the aromatic ring has directing effect on the position of the ~SO_3H group insertion. The positive induction effect of alkyl substituent generally increased the electron density in the ortho and para position. However, the steric effect had the main influence on the ratio of ortho and para isomers. The amount of the ortho isomer equally decreases with increasing steric volume of substituent on the aromatic ring (Table 1.1). The yields of ortho, meta and para isomers by heterogeneous sulfonation of alkylbenzenes using H_2SO_4, HSO_3Cl, SO_3 (g) were showed in Table 1.2.

Table 1.1 *The steric effect influence of alkyl chain on the ortho/para ratio [10]*

Nitration of	ortho [%]	para [%]
methylbenzene	61	39
ethylbenzene	47	53
isopropylbenzene	31	69
terc.butylbenzene	18	82

Table 1.2 *The yields of heterogeneous sulfonation of alkylbenzenes [15, 16]*

Sulfonation of	Agent	Temperature [°C]	Yield of isomers		
			ortho	meta	para
methylbenzene	H_2SO_4	25	27.9	1.3	70.8
ethylbenzene	H_2SO_4	25	19.4	3.9	76.7
isopropylbenzene	H_2SO_4	25	7.4	3.9	88.7
methylbenzene	HSO_3Cl	25	11.6	3.2	85.2
ethylbenzene	HSO_3Cl	25	6.4	1.6	92.0
isopropylbenzene	HSO_3Cl	25	2.8	1.9	95.3
toluene	SO_3 (g)	25	15.3	4.9	79.8
toluene	SO_3 (g)	50	12.2	9.5	78.3

1.3 Sulfonation of polymers containing aromatic ring

1.3.1 Homogeneous sulfonation of polymers

Homogeneous sulfonation of PS has been firstly carried out in a chloroform solution at −20°C using SO_3 or HSO_3Cl as sulfonating agents [17, 18].

Turbak [19] sulfonated poly(vinyltoluene) and polystyrene in the homogeneous phase without significant crosslinking by using higher complexes of SO_3 with triethyl phosphate as sulfonating agents.

Makowski et. al. [20] prepared a lightly sulfonated polystyrene by a reproducible reaction of dichloroethane solution of polystyrene with acetyl sulfate at a temperature of 50°C for 1 hour. Acetyl sulfate as the sulfonating agent was prepared by mixing concentrated sulfuric acid and acetic anhydride in solution of dichloroethane at temperatures lower than 10°C. The sulfonated product was isolated by steam stripping and pulverized with water in a high-speed mixer for liquids, then the SPS was filtered and vacuum oven dried. Obtained sulfonated polystyrene contained from 0.1 to 1.3 wt % of sulfur.

Makowski et. al. [20] sulfonated also a t-butyl-styrene-isoprene copolymer using complexes of SO_3 and $(EtO)_3PO$ dissolved in a methylene chloride.

Weiss [21] sulfonated triblock copolymer of poly(styrene-ethylene/butylene-styrene) (M_w=50 000) up to a concentration of the ~SO_3H groups of 18 mole % using acetyl sulfate and dichloroethane solution of copolymer.

The sulfonation of polyphenylene oxide (PPO) [22, 23] was conducted in chloroform ($CHCl_3$) by using chlorosulfonic acid ($ClSO_3H$) as the sulfonating agent.

Huang and Kim [24] sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) by using chlorosulfonic acid and solution of the copolymer in chloroform, and then neutralized it by forming a sodium salt. The kinetics of the sulfonation reaction depended on both reactants concentration and the reaction was irreversible.

The sulfonation reaction of model compounds of diene monomers used in EPDM rubber was studied by Thaler [25]. The sulfonation of small molecular models of EPDM (such as ethylidenenornbornane (ENB), dihydrodicyclopentadiene (DCPDH)) was reported.

Thaler and de Brevil [26] attempted to determine the mechanism of sulfonation reactions on other models of noncyclic olefins such as 3-hexene, 1-butene (II) and cyclic olefins such as cyclopentene, dihydrodicyclopentadiene, ethylidene cyclopentene and ethylidene cyclohexane (III) in ^{13}C-NMR studies.

The preparation of sulfonated ethylene-propylene elastomer (EPDM) by continuous process in an extruder was achieved by Siadat et. al. [27]. The copolymer was initially heated to 85°C under a nitrogen atmosphere in a single-screw extruder reactor. Then sulfuric acid and acetic anhydride were fed into the extruder.

Jin et. al. [28] sulfonated poly(ether-ether-ketone) (PEEK) by the reaction of PEEK and concentrated sulfuric acid and prepared its sodium and zinc salts ranging from 4 to 100 mole % of substitution. Crosslinking reaction has not been observed in the presence of water during the sulfonation reaction.

Zhou et. al. [29, 30] prepared sulfonated polyisoprene in a very diluted solution of chloroform by the reaction with acetyl sulfate.

Vink [31] prepared sulfonated polystyrene (SPS) by using a homogeneous reaction of a PS solution in cyclohexane with a mixture of concentrated H_2SO_4 and phosphorous pentoxide (P_4O_{10}) to yield 95 mole % ~SO_3H.

Thaler [32] sulfonated PS by using fatty acid sulfates of a higher molecular weight as the sulfonating agents. Lauric (C_{12}) and stearic (C_{18}) acids were treated with liquid SO_3 (or $ClSO_3H$) to form cyclohexane soluble agents.

1.3.2 Heterogeneous reaction of polymers sulfonation

Although a little has been published about preparation of SPS via sulfonation in the heterogeneous phase, this method is assumed advantageous over the homogeneous processes described earlier, because it avoids problems with solvents and the separation of a sulfonated product from the reaction mixture. The heterogeneous sulfonation reaction, i.e., solid-liquid (s–l) (such as PS–H_2SO_4) or solid-gas (s–g) (such as PS–SO_3), can be used in commercial process yielding cheap sulfonated ionomers from waste polymers.

Kim et. al. [33] described a method which utilized monodisperse crosslinked PS beads as the substrate. Treatment with gaseous SO_3 above fuming sulfuric acid was used to sulfonate these PS beads. Monodisperse PS beads (450 nm in diameter) were sulfonated in the gaseous phase for 3 days at room temperature to obtain yellowish sulfonated product. Kim's paper is the only reference dealing with the (s–g) heterogeneous sulfonation method of PS found in literature.

Regas [34] sulfonated polystyrene-divinylbenzene networks (M_w from 1 000 to 50 000) by reaction of crosslinked polystyrene-divinylbenzene beads swollen in dichloroethane with concentrated H_2SO_4 at 80°C for about 10 min and with the $ClSO_3H$ at 0°C.

Carrol et. al. [35] developed (s–l) heterogeneous sulfonation of a finely divided PS powder ($M_w = 240\ 000$). The PS powder was prepared by precipitation of a diluted PS solution in 2-butanone with methanol. Sulfonation of this PS powder was carried out with 100 % H_2SO_4 as the sulfonating agent in the presence of Ag_2SO_4 as a catalyst at room temperature for 10 min. The Ag_2SO_4 has prevented the formation of side products in this reaction. The 100 % yield of the sulfonation reaction was achieved within 5–15 min. It seems, that mono-substitution at the para-position was the only reaction proceeding in the described process.

Bishop et. al. [36] investigated the behavior of diluted solutions of poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) in strong acids (i.e. H_2SO_4, HSO_3Cl). A crosslinking was observed due to side reaction accompanying the sulfonation process.

2 AIM OF THE THESIS

The aim of this work is, first of all, to develop a method for preparation of SPS by heterogeneous reaction technique of porous foamed PS particles or solid PS beads with gaseous SO_3 in a mixture with air. In order to relate results from heterogeneous sulfonation to the published data, the homogeneous technique of sulfonation will also be studied. Isolation of highly sulfonated SPS prepared by heterogeneous technique can be achieved more easily than from solution. Possibility of continuous heterogeneous sulfonation process makes this method more advantageous for eventual industrial SPS manufacturing. The possible industrial application of SPS seems in building industry for preparation of concrete with special properties.

On the basis of the current state of the art, experimental program was focused on the following goals:

(i) Preparation of highly sulfonated PS using homogeneous sulfonation technique and attempt to isolate the highly sulfonated water-soluble polystyrene from reaction mixture.

Only a lightly, water insoluble sulfonated polystyrene (below 10 mole % of ~SO_3H) was mentioned in processes based on homogeneous sulfonation by Makowski [20]. Problems with preparation of pure high sulfonated PS were solved by the evaporation of solvents to isolate the SPS and further purification of the resulting SPS.

(ii) Preparation and characterization of PS particles suitable for heterogeneous sulfonation.

Several types of PS particles with different specific surface area were used in experimental program of heterogeneous sulfonation technique. Finely divided PS fluff formed by milling of solid PS, commercial PS beads and pellets, commercial foamed PS and PS powder precipitated from PS solution were used in the experimental work. The surface area of prepared PS samples was determined by BET measurements or sieve analysis, the morphology was studied using electron scanning microscopy (SEM).

(iii) Heterogeneous sulfonation technique using gaseous SO_3 (or H_2SO_4) and various types of PS particles.

First method was the s–g heterogeneous reaction of solid PS with gaseous mixture SO_3 in nitrogen as carrier-gas for sulfonating agent. These experiments were focused to study dependence of sulfonation rate on specific surface area and to attempt of preparation of highly SPS (and eventual the water soluble SPS). Optimalization of several reaction conditions (such as reaction time, reaction temperature, choice of PS) could be attempted in order to obtain the most balanced results of sulfonation. In addition, sulfonation of the foamed PS is intended for investigation.

Second method of sulfonation was based on the s–l heterogeneous reaction between solid PS and liquid sulfuric acid. These second sulfonation heterogeneous method seems less advantageous than the s–g reaction by reason of difficult product separation and purification from the reaction mixture.

(iv) Modification of concrete materials with SPS.

An effect of prepared sulfonated materials on the mechanical properties such as tensile and compressive strength of the modified concrete mixtures compared to the unmodified concrete was tested.

3 EXPERIMENTAL METHODS

3.1 Sulfonation reactions

3.1.1 Homogeneous sulfonation

The homogeneous sulfonation of PS was carried out in solution of DCE at about 50°C using acetyl sulfate as sulfonating agents. The sulfonation reaction was terminated by addition of 20 ml water and the sulfonated polymer was separated using precipitation with water or by evaporation of solvent (Method A). The purification of water-soluble SPS was based on the neutralization of raw SPS with precipitated $CaCO_3$ powder in ethanol solution. The excess of $CaCO_3$ and insoluble impurities were filtered and neutralized polymer in the form of Ca^{2+} salt was isolated after evaporation of solvent.

3.1.2 Heterogeneous sulfonation

The PS was exposed to the SO_3 vapors above the fuming oleum in the joined flask. The experiment was carried out at laboratory temperature for 2 and 12 hours (Method B). More sophisticated sulfonation procedure was utilized in preliminary study of sulfonation kinetics using special absorption tower with sintered glass at the bottom and continuous source of gaseous SO_3 (Method C). After the reaction was stopped, non-chemically bonded SO_3 was removed by washing SPS with water. The final experimental set up used for heterogeneous sulfonation consist of the source of gaseous mixture of SO_3 + N_2 (flow rate approximately 170 $cm^3.min^{-1}$) and of the sulfonation reactor equipped with PTFE-glass blender and with input/output valves for sulfonating agent (Method D). The sulfonation experiments were summarized in Table 3.1.

Table 3.1 *Summary of the sulfonation experiments*

Method	Technique	PS	M_w	Sulfonation agent	Temp. [°C]	Time [min]	Solvent
A	Homogeneous	Krasten 127/9001	180000	acetyl sulfate	50	60	DCE
A	Homogeneous	PS	3000 200000 2000000	acetyl sulfate	50	15 - 360	DCE
A	Homogeneous	Krasten 127/9001	180000	acetyl sulfate	22	120	DCE
B	Heterogeneous	milled Krasten 127/9001	150000	SO_3 (g)	22	120 720	none
C	Heterogeneous	milled Krasten 127/9001	150000	$SO_3(g) + N_2(g)$	22		none
D	Heterogeneous	pellets Krasten 127/9001	180000	$SO_3(g) + N_2(g)$	-5 22, 50	60 - 1440 5 - 1440	none
D	Heterogeneous	beads Krasten 127/9001	180000	$SO_3(g) + N_2(g)$	22	5 - 180	none
D	Heterogeneous	milled Krasten 127/9001	150000	$SO_3(g) + N_2(g)$	22	5 - 1440	none
D	Heterogeneous	PS foamed	—	$SO_3(g) + N_2(g)$	22	5 - 1440	none
D	Heterogeneous	PS powder No.1 Krasten 127/9001	180000	$SO_3(g) + N_2(g)$	22	3 - 30	none
D	Heterogeneous	PS powder No.2 Krasten 127/9001	180000	$SO_3(g) + N_2(g)$	-5, 22, 50	5 - 1440	none
D	Heterogeneous	PS	3000 200000 2000000	$SO_3(g) + N_2(g)$	22	15 - 360	none

3.2 Preparation of concrete materials modified using SPS

Polymer-concrete material with addition 10 vol % and 20 vol % of sulfonated foamed PS and unsulfonated foamed PS were prepared. The concrete samples without polymer additions were prepared to comparison. The dry components were mixed in a laboratory blender at first, the foamed PS was mixed into concrete mixture commonly with the quartz sand and with cement. Then water was added, different volume of water was fitted to achievement approximately same consistence in all the prepared concrete mixtures. Water/Portland cement (W/C) ratio ranging from 0.37 to 0.56.

3.3 Characterization methods

In order to determine sulfonation levels an alkalimetric titration, ICP atomic emission spectroscopy and FT-IR spectroscopy were used. The elemental analysis of SPS particles was determined by EDAX microanalysis. The FT-IR spectra were used to indicate the $\sim SO_3H$ group qualitatively. The molecular weight of starting PS was measured using an Ubbelohde viscometer. The thermal stability was studied by thermogravimetric analysis (TGA). The scanning electron microscopy (SEM) was used to study of heterogeneous sulfonation of PS particles. The mechanical properties of concrete samples could be tested by measurement of compressive strength and tensile strength using laboratory press.

4 THE MAIN RESULTS OF THIS WORK

4.1 Characterisation of polystyrene (PS)

4.1.1 Specific surface area of PS particles

The experimental values of specific surface area of PS powder, determined by BET measurement and by sieve analysis were showed in Table 4.1.

Table 4.1 *Summary of the specific surface area of PS particles*

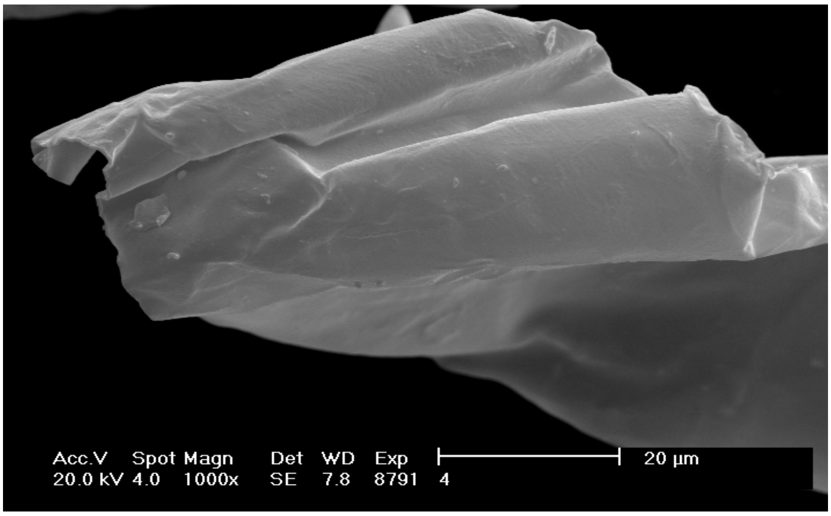
No.:	PS material description	Specific surface area $[m^2.g^{-1}]$
PS 2	PS beads (Krasten 127/9001)	0.017
PS 3	milled PS (Krasten 127/9001)	0.96
PS 4	crushed foamed PS	11.18
PS 5	PS powder (Krasten 127/9001)	33.37

4.1.2 The morphology of PS particles

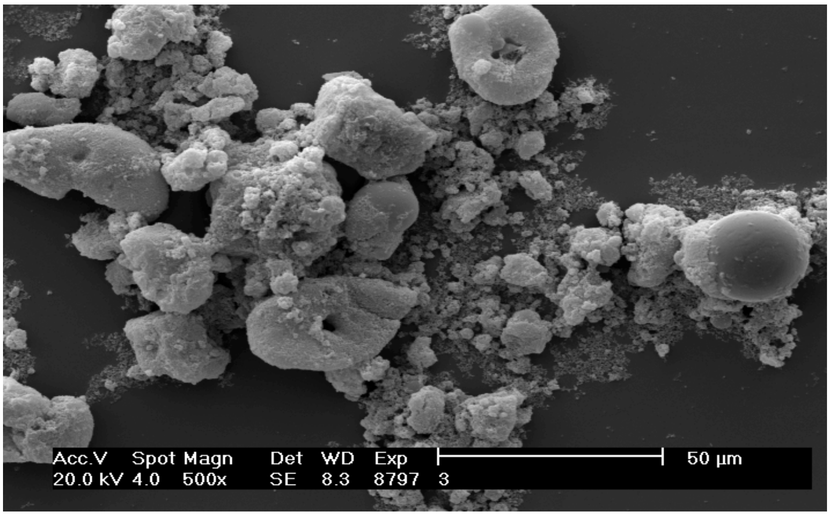
The size of the spherical beads, formed by the suspension polymerization of styrene, ranging from 250 to 450 μm, the average size of milled PS beads was approximately 100 μm. The shape of particles obtained by milling Krasten beads under decreased temperature was lightly irregular and thermoplastic change was observed on the surface. The size of the PS particles, formed by crushing of foamed PS (Figure 4.1.a) was also about 100 μm; the deformed sheet-like shape of crushed foamed PS particles was observed. The particles of PS powder (Figure 4.1.b), prepared by precipitation, occurred as strongly deformed beads with broad distribution of sizes, which ranged from approximately 5 to about 30 μm.

Important structural parameter, which has influence on the rate of sulfonation, seems be the specific surface area of particles. The smooth surface of PS beads with random occurrence of irregularities of size about 1μm was observed. The surface of milled PS was distorted with marked cracks, but specific surface was not substantially increased compare to PS beads surface. The foamed PS particles had a very smooth surface. Anomalous is the very porous surface of PS powder particles. It could be speculated, that the small interstitial species on the PS powder surface, with size of about 10^{-1} μm, can be linked to the size of random coil of PS macromolecules. This effect could cause the substantial difference in the rate of sulfonation for PS powder compare to another three kinds of PS particles. The reactivity is probably affected with the higher surface area of PS powder particles, which caused easily access of the sulfur trioxide to PS substrate.

Figure 4.1 *The morphology of PS particles (page 1)*



(a) PS particles prepared by crushing of foamed PS; magnification 1000×



(b) PS powder prepared by precipitation; magnification 500×

4.2 Homogeneous sulfonation reaction

4.2.1 Kinetics of homogeneous sulfonation of PS

Sulfonated SPS with various ~SO_3H content was prepared by homogeneous sulfonation utilizing acetyl sulfate in dichloroethane (DCE) at 50°C for 1 hour. The results of SPS analysis and calculated ~SO_3H content were summarized in Table 4.2.

***Table 4.2** Sulfonated polystyrenes prepared by homogeneous sulfonation*

Designation of sample	$x_{theoretical}$(~SO_3H) [mole %]	ω(S) [%]	$x_{practical}$(~SO_3H) [mole %]
SPS 0.5	9.4	2.93	10.3
SPS 1	18.7	4.09	14.8
SPS 2	37.5	6.02	23.0
SPS 3	56.2	6.77	26.5
SPS6	112.45	13.89	69.1

The FT-IR spectra of SPS were used to indicate the ~SO_3H group qualitatively. The occurrence of peak of ~SO_3^- symmetric stretching vibration at 1040 cm^{-1} and ~SO_3^- asymmetric stretching vibration at 1180 cm^{-1} proved qualitatively the presence of the attached ~SO_3H groups in each of sulfonated samples. Also the appearance of the vibration of substituted benzene ring at 1130 cm^{-1} and the non-plane deformation of substituted benzene ring γ(C–H) at 840 cm^{-1} validated the aromatic ring substitution. On the other hand, there was not found the S–H vibration around wavenumbers 2550 – 2600 cm^{-1}.

In this study, effect of molecular weight of the used PS on the degree of sulfonation was also investigated. The time dependence of the sulfonation yield for three different M_w was shown in Figure 4.2. M_w of the PS samples used varied over three orders of magnitude, assuming M_w affects the size of the random coil and, thus, the access of SO_3 to PS aromatic rings. It was assumed that the influence of the molecular weight of starting polymer on the sulfonation rate was caused most likely by steric hindrances of aromatic rings caused by coiled polymeric chain.

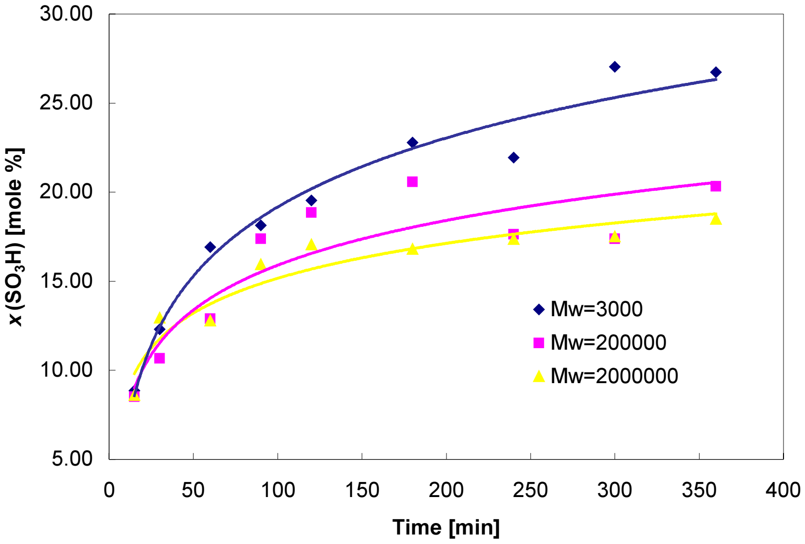


***Figure 4.2** Extent of sulfonation versus reaction time for PS with different M_w*

The study of homogeneous sulfonation reaction resulted in reaction mechanism depicted in Figure 4.3. At first, the acetyl sulfate was formed by reaction of acetic anhydride with sulfuric acid, the sulfonating agent was not from acetic acid further purified. Second reaction depicted was the actual sulfonation reaction, when the sulfonic groups were attached along the polymeric chain statistically.

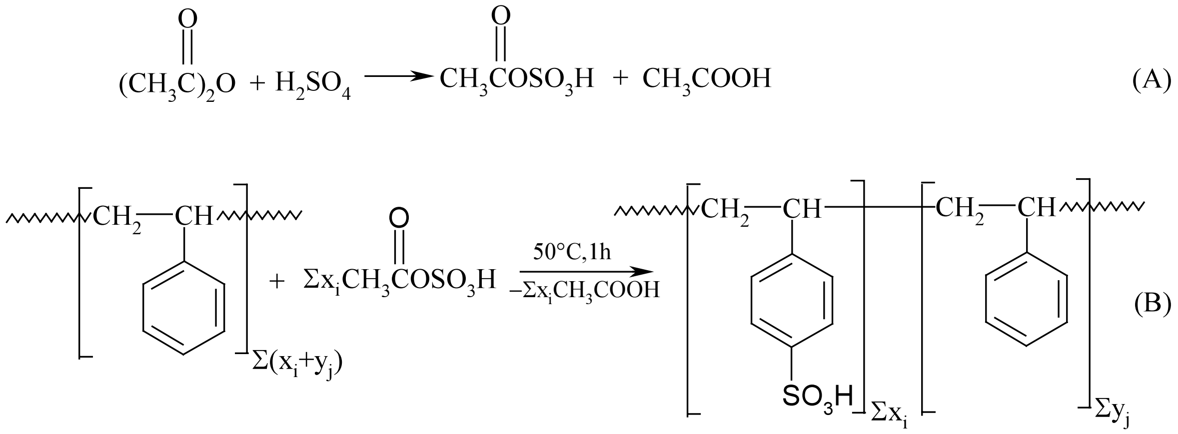


Figure 4.3 *Reaction scheme of homogeneous sulfonation:*
(A) Acetylsulfate generation
(B) Sulfonation of PS in solution of DCE

The sulfonation reaction could be accompanied with the sulfone formation by the following crosslinking reaction between two sulfonic groups of different SPS molecules. The most probable crosslinking reaction mechanism was shown in Figure 4.4. The tendency to crosslinking reaction is probably increased with increasing content of sulfonic groups, with increasing concentration of the sulfonating agent in polymer solution and also with increasing reaction temperature.

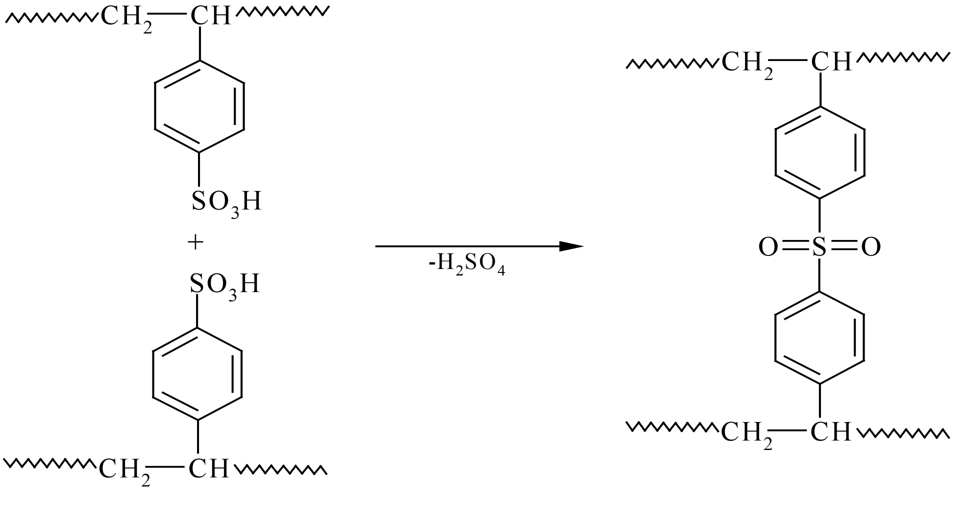


Figure 4.4 *Crosslinking reaction of SPS*

The homogeneous sulfonation, depicted in Figure 4.3 proceeds by the reaction mechanism of second order, and experimentally determined amounts of SPS were fitted by means of Equation 4.1.

$$\frac{x_t(SO_3H)}{100\cdot\left(100-x_t(SO_3H)\right)}=k\cdot t \tag{4.1}$$

The apparent deviation of experimental data from the linear relationship of the reaction kinetics of second order was probably caused by two stage of sulfonation reaction. The sulfonation was occurred on the available surface position of the PS random coil in the initial stage of reaction. Then the diffusion of sulfonating agent into the polymeric coil affected the rate of sulfonation in second stage. The increased size of random coil of PS molecules in solution could cause decrease the rate constant. The rate constants of homogeneous sulfonation for each M_w were calculated as tangent of time dependence of reciprocal amount of PS (Figure 4.5) and value of rate constants were presented in Table 4.3

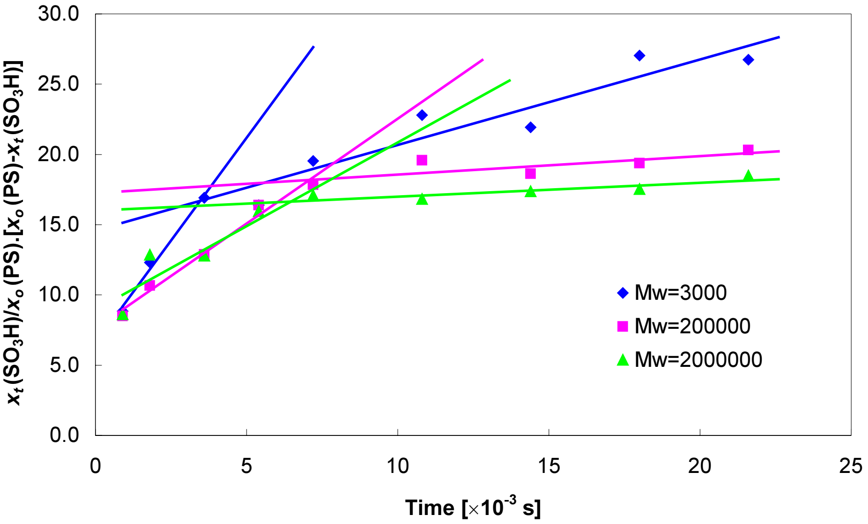


***Figure 4.5** The kinetics of homogeneous sulfonation of PS with M_w=3000, 200 000 and 2 000 000*

***Table 4.3** The rate constants of homogeneous sulfonation of PS solution in DCE using acetyl sulfate at 50°C*

M_w	k_1 [×10^3 mole %$^{-1}$.s^{-1}]	k_2 [×10^3 mole %$^{-1}$.s^{-1}]
3000	2.9286	0.6084
200000	1.4908	0.1317
2000000	1.1923	0.0983

4.2.2 Preparation of water soluble sulfonated polystyrene

The soluble sulfonated PS was prepared by homogeneous (l–l) sulfonation in DCE using small excess of acetylsulfate as sulfonating agent. Sulfonation reaction was carried at 50°C for 2 hours. The water-soluble sulfonated polystyrene appearance was a dark yellow powder. The sulfonated polymer was characterized by very good solubility in water, methanol and ethanol at laboratory temperature. The sulfur content of prepared water soluble PS was determined by ICP measurement to reach 12.24 wt. %, which corresponded to 72.9 mole % of sulfonic groups. The degree of crosslinking was negligible because SPS exhibited good solubility in all solvents used. The qualitative FT-IR analysis (in Figure 4.6.) showed presence of the vibration of symmetric and asymmetric stretching vibration of sulfonic group at 1040.0 cm^{-1} and 1181.5 cm^{-1}. The complete spectrum was in a good agreement with the spectrum of sodium salt of sulfonated polystyrene obtained from Aldrich (prepared by emulsion polymerization of sodium salt of sulfonated styrene).

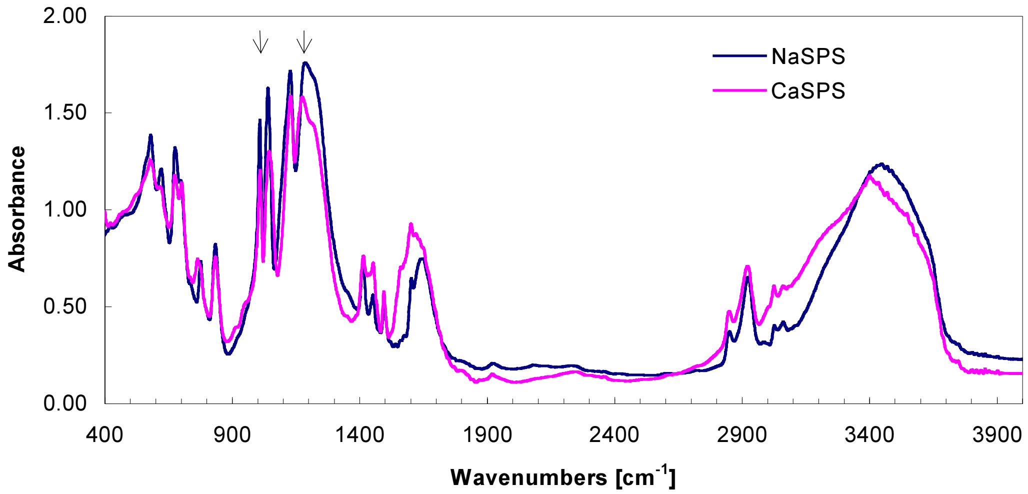


Figure 4.6 *FT-IR spectra of water-soluble calcium and sodium salt of polystyrenesulfonic acid*

4.3 Heterogeneous sulfonation

4.3.1 The heterogeneous (s-g) sulfonation of polystyrene powders

Sulfonation kinetics for the heterogeneous solid-gas polystyrene sulfonation was studied. Results of the first attempt to sulfonate PS in (s–g) phase are shown in Table 4.4.

Table 4.4 *Heterogeneous sulfonation of milled Krasten 127*

Designation of sample	Sulfonation time [h]	$\omega(S)$ [%]	$x(SO_3H)$ [mole %]
PS 1	2	0.32	1.06
PS 2	12	2.45	8.48

In addition to the milled PS, several other forms of PS with different specific surface area were used in (s–g) sulfonation applying Method D. The results of analysis were shown in Figure 4.7. as a dependence of sulfonation level on the reaction time. The experimental data suggested that the sulfonation rate was slightly increased with increased specific surface area for beads, milled beads and foamed PS. Again, the main effect of specific surface area of the reacted solid PS seemed to increased equilibrium sulfonation level with increasing specific surface area. The precipitated powder showed substantially different behavior. The morphological observation showed that the surface morphology was most probably the reason for the observed rapid sulfonation of this PS.

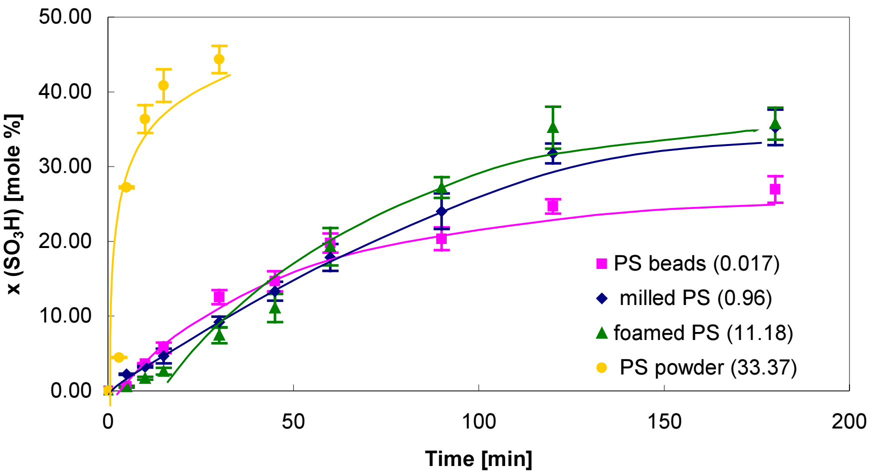


Figure 4.7 *Extent of sulfonation versus time of reaction for sulfonated polystyrenes(with different specific surface area in parentheses [$m^2.g^{-1}$])*

The FT-IR spectra of sulfonated PS powders were taken over a range of wavenumbers from 400 to 4000 cm^{-1} (Figure 4.8). These spectra indicated the enhanced content of sulfonic group in the course of sulfonation (peaks of the vibration of sulfonic group at approximately 1040 and 1180 cm^{-1}). For the analysis of sulfonic group, spectra were collected also over a range from 920 to 1380 cm^{-1} (Figure 4.9). The study of FT-IR spectra in the entire wavenumber interval suggested the bonding of sulfonic group on PS aromatic ring (peaks of non-plane deformation of substituted aromatic ring $\gamma(C_{ar}–H)$ at wavenumbers approximately from 830 to 850 cm^{-1}). On the other hand, the presence of the vibrations of ν(S–H) (2550–2600 cm^{-1}) and ν(S–S) (400–500 cm^{-1}) were not found in the FT-IR spectra. Although the increased occurrence of crosslinking was proposed with increased temperature, peaks located at the same wavenumbers, however of different intensity, were observed in the FT-IR spectra of PS powders sulfonated at three temperatures for 12 hours. This fact was expected by the interference of vibration $Ar–SO_2–Ar$ (1328 and 1162 cm^{-1}) and vibration of ν_{as}(S–O) (at 1180 cm^{-1}) into a very broad peak at approximately 1100 cm^{-1} – 1350 cm^{-1}.

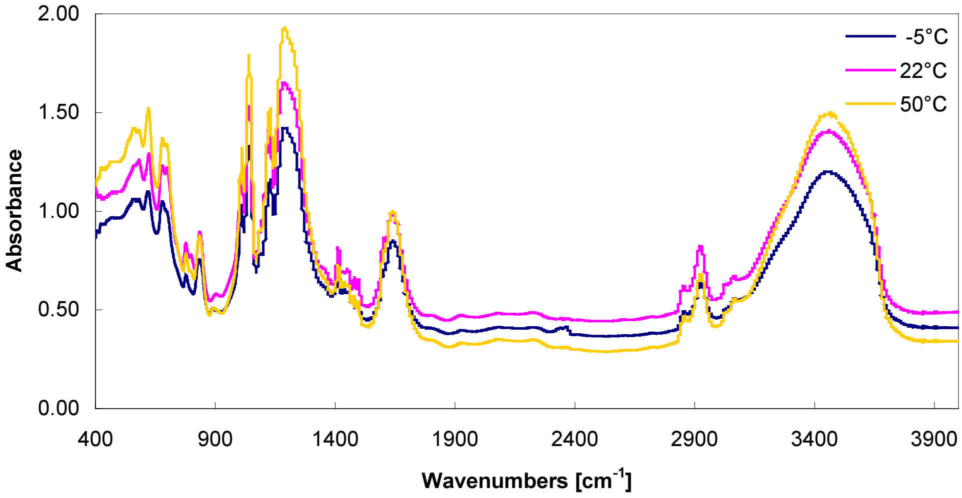


Figure 4.8 *FT-IR spectra of sulfonated PS powder for reaction time 12hours*

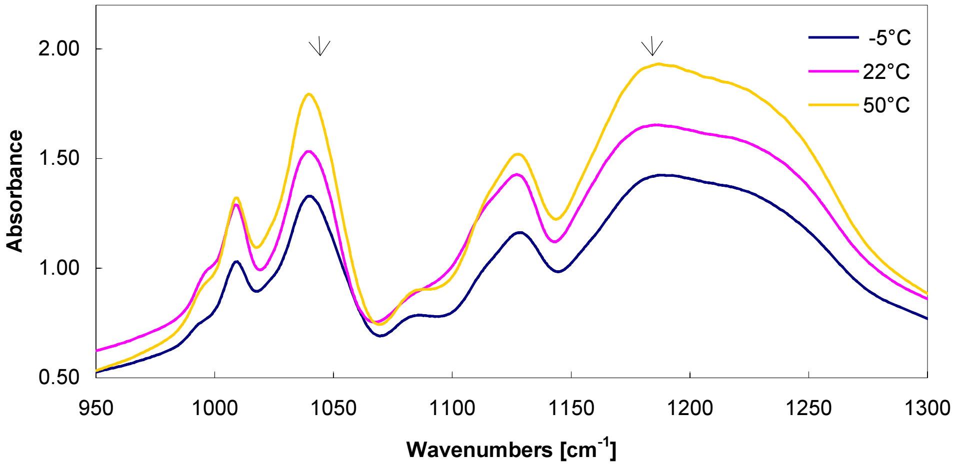


Figure 4.9 *FT-IR spectra of sulfonated PS powder for reaction time 12 hours*

4.3.2 Crosslinking during the heterogeneous sulfonation

The undesirable property of sulfonic group attached is the formation of sulfone by reaction between two sulfonic groups (Chapter 1). The reacting sulfonic groups can attach to either one or two molecules of sulfonated PS. Intermolecular reaction, of several sulfonic groups along the polymer backbone brought about formation of polymeric network or, at least, gels, which caused insolubility of sulfonated polymer and the polymer was swelled only. The SPS prepared by heterogeneous sulfonation reaction was substantially swollen in water, methanol and ethanol. The insolubility of prepared SPS samples was assumed sufficient evidence to establish the presence of crosslinking reaction.

The calculation of content of sulfone bridges based on the elemental sulfur, sodium and calcium ions analysis was attempted. The ICP spectroscopy was used to determine the elemental composition of sulfur and counter ions (Na^+, Ca^{2+}) in the SPS samples prepared by heterogeneous sulfonation of precipitated PS at three different reaction temperature (-5°C, 22°C, 50°C). The results of elemental analysis measured by the ICP spectroscopy are shown in Figures 4.10 – 4.11 The sulfur content increased with the increasing temperature, the highest sulfur content was determined for SPS sample prepared at the highest temperature. The content of sodium was higher then theoretically calculated value based on the sulfur analysis, however it gave about approximate estimation of temperature dependence of sulfone bridge formation. The increasing content of sodium ions with increasing temperature was assumed, however the sodium content decreased with increased temperature. A hypothesis that content of sulfone bridges in SPS increased with increased sulfonation temperature was proposed, based on the above described evidence.

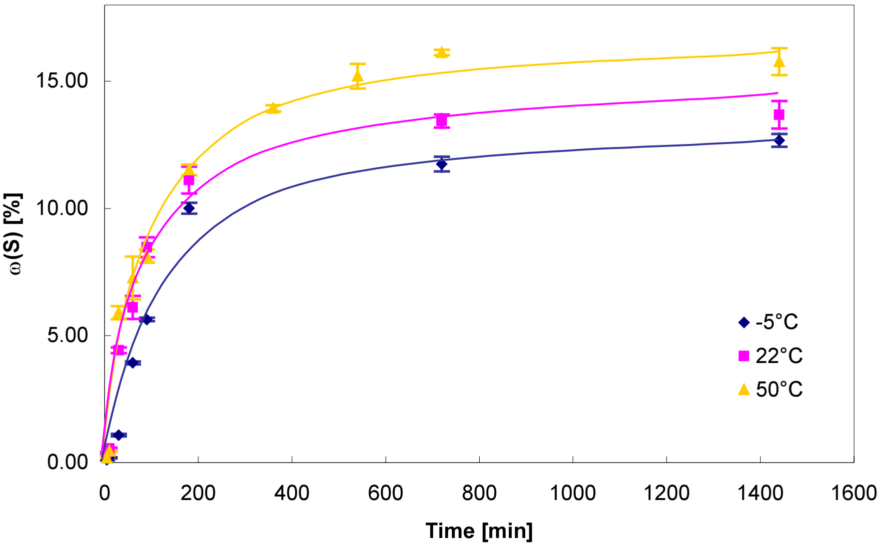


Figure 4.10 *The dependence of sulfur content on sulfonation time of PS powder*

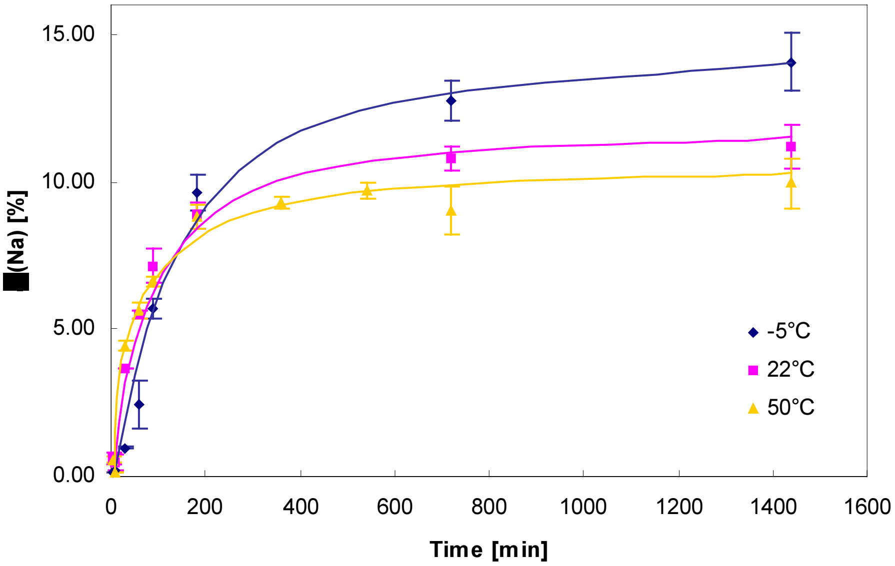


Figure 4.11 *The dependence of sodium content during course of sulfonation*

On the basis of ascertained facts, the reaction scheme of heterogeneous sulfonation reaction was proposed (Figure 4.12). In agreement with the model of sulfonation of ethylbenzene, the SO_3 reacts with PS to form the para-polystyrenesulfonic acid. In reason of both the positive inductive effect of polymeric backbone and, above all, the steric hindrance, the para-position of attached sulfonic groups location were preferred. The influence of entanglements causes the non-statistical distribution of sulfonic groups along the polymeric chain. The formed sulfonic groups (in the possible presence of the SO_3) participated in the crosslinking reaction to form the totally crosslinked SPS with probably high content of the sulfone bridges. This fact was recognized in the attempts dissolve the SPS in water, when only a gel was formed.

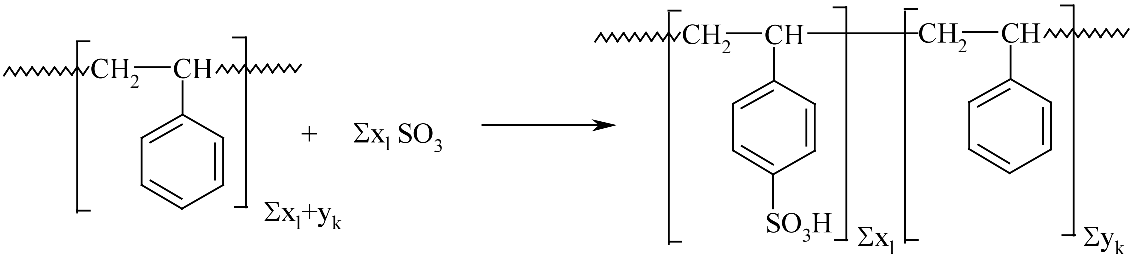


Figure 4.12 *The general reaction scheme of heterogeneous sulfonation utilizing SO_3*

Although the homogeneous sulfonation proceeds as the second order reaction, the concentration of SO_3 was approximately constant during heterogeneous sulfonation and rate constants of heterogeneous sulfonation can involve SO_3 concentration. Then, the kinetic data of heterogeneous sulfonation of precipitated PS using gaseous SO_3 can be processed by assuming the reaction mechanism to be the first order reaction. The influence of diffusion into PS powder was due to the morphology of PS particles negligible in the initial stage of sulfonation. On the basis of this fact, the influence of diffusion was not accounted for the initial sulfonation rate calculations. Equation 4.2 described the proposed kinetics of heterogeneous sulfonation.

$$\ln\frac{1}{1-x(SO_3H)} = k\cdot t \tag{4.2}$$

The reaction rate was approximately constant for the first 180 minutes for each of the three temperatures and then began to level off in the course of continuous sulfonation due to both the decreasing PS surface and the growing influence of diffusion of SO_3 into PS particles. The results of sulfur analysis for PS samples sulfonated in time interval from 0 to 180 minutes were used as kinetic data for rate constants determination,data were shown in Figure 4.13.

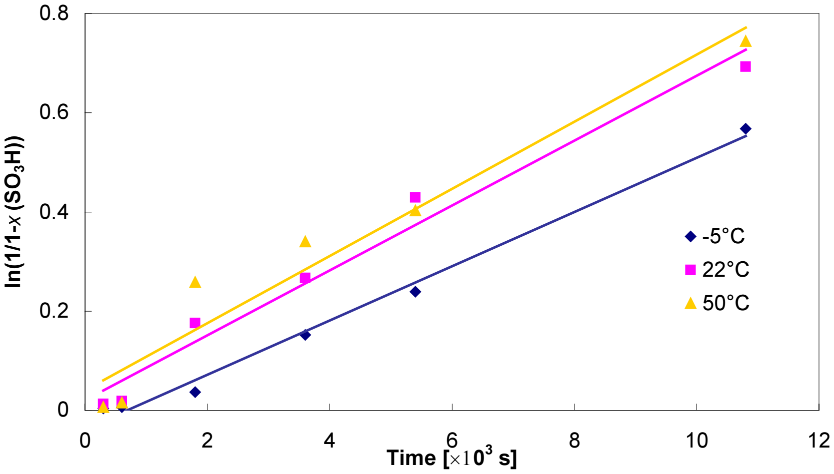


Figure 4.13 *The kinetics data of heterogeneous sulfonation of PS powder utilizing SO_3*

The three values of rate constant of PS powder heterogeneous sulfonation were calculated from the slope of the lines for three different temperatures and were shown in Table 4.5.

The values of rate constant for heterogeneous were substantially lower than in the case of homogeneous sulfonation and rate constants were lightly increased with increasing temperature from –5°C to 50°C.

Table 4.5 *The rate constants of heterogeneous sulfonation of PS powder using SO_3 at –5, 22 and 50°C*

Temperature [°C]	k [$\times 10^3$ s^{-1}]
-5	0.5471
22	0.6542
50	0.6774

4.3.3 Kinetic study of heterogeneous sulfonation reaction on solid PS surface

In order to investigate depth of (g–s) sulfonation, SEM and EDAX microanalysis measurements were performed. The description of SEM photographs of sulfonated layers were shown in Figure 4.14.

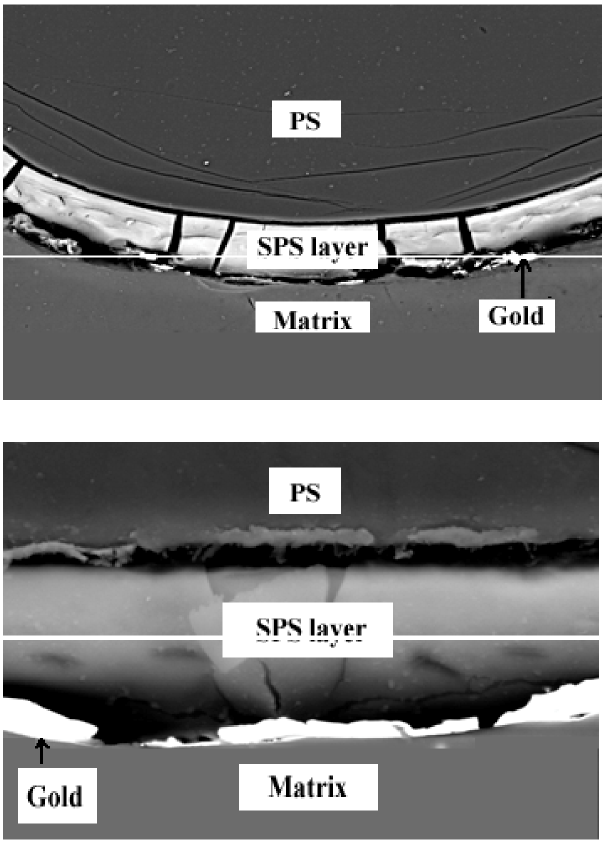


Figure 4.14 *The SEM photographs of SPS layer at magnification 200× (above) and detail of SPS layer at magnification 2000× (below)*

The morphological investigations of the sulfonated PS particles showed that PS changes its contrast upon sulfonation resulting in a formation of a distinct layer of sulfonated PS visible on the cross section of sulfonated particles. The results of thickness measurement of sharply defined sulfonated layer on the PS pellets surface obtained from SEM measurements are shown in Figure 4.15.

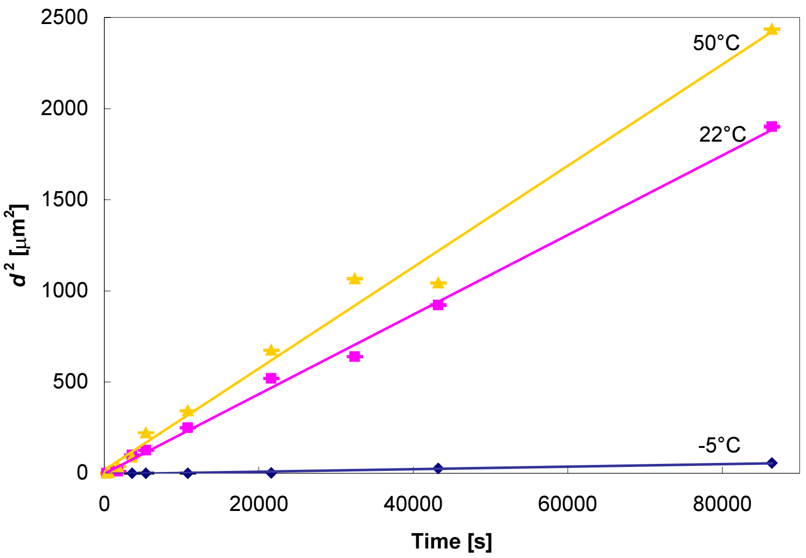


Figure 4.15 *The linear relationship between the square of average layer thickness and time of heterogeneous sulfonation at different reaction temperatures (see Equation 5.10)*

The increase of sulfonated layer thickness on the solid PS surface was described using Equation 4.3:

$$d = (D \cdot t)^{1/2} \ , \qquad (4.3)$$

where	D	is the diffusion coefficient	[μm.min^{-1}],
	d	is the sulfonated layer thickness	[μm].

The calculated diffusion coefficients of SO_3 into partially sulfonated PS for temperature –5°C, 22°C and 50°C were summarized in Table 4.6.

Table 4.6 *The diffusion coefficients of gaseous SO_3 into the solid PS particles*

T [°]C	D [× 10^{10} cm^2.s^{-1}]
-5	0.07
22	2.18
50	2.78

The activation energy of diffusion was calculated from Arrhenius equation[37, 38]:

$$D = A \cdot e^{-E_{aD}/RT} \ , \qquad (4.4)$$

where	A	is the pre-exponential factor	[cm.s^{-1}],
	E_{aD}	is the activation energy of diffusion	[kJ.mol^{-1}].

The activation energy of diffusion was estimated from experimental data plotted in Figure 4.16. The value of activation energy of diffusion was calculated using Equation 4.4 as $E_{aD} = 49.13$ kJ.mol^{-1} and the pre-exponential factor as $A = 4.12 \cdot 10^{-6}$ cm^2.s^{-1}.

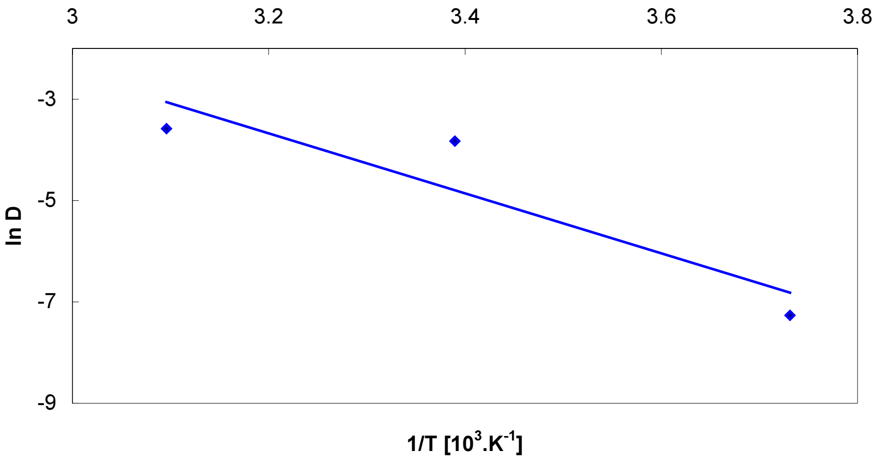


Figure 4.16 *Linear relationship between the logarithm of diffusion coefficient and the inversion value of temperature*

The experimentally determined average values of the yield of sulfonation in sulfonated layer (S_x), obtained by means of EDAX analysis of the sulfonated layers, were summarized in Table 4.7.

Table 4.7 *The sulfonation degree (S_x) related to one aromatic ring obtained by means of scanning electron measurement of sulfonated PS pellets prepared at temperature approximately -5°C, 22°C, 50°C*

Time [min]	5	10	30	60	90	180	360	720	1440
$\overline{S_x}$ (-5°C) [mole %]	–	–	–	0.14	0.14	0.24	0.36	0.57	0.84
$\overline{S_x}$ (20°C) [mole %]	0.20	0.30	0.43	0.36	0.41	0.43	0.50	0.57	0.48
$\overline{S_x}$ (50°C) [mole %]	(0.26)	0.46	0.65	0.57	0.58	0.72	1.01	0.79	(1.24)

In the processing of experimental data and analysis of the kinetics of the heterogeneous sulfonation of PS, the general Johanson-Mehl-Avrami-Jerofyeev-Kolgomorov's (JMAJK) equation was used [39, 40]:

$$-\ln(1-\alpha) = k \cdot t^m , \tag{4.5}$$

where			
	α	is the conversion defined as the volume ratio of the sulfonated part of PS particles to the total PS particle	
	k	is the overall rate constant of the sulfonation reaction	[s^{-1}]
	m	is the exponent factor.	

For the cylindrical PS pellets was the conversion expressed in Equation 4.6:

$$\alpha = 1 - \frac{(r_o - d)^2 \cdot (v_o - 2d)}{r_o^2 \cdot v_o}, \tag{4.6}$$

where			
	r_o	is the average radius of starting cylindrical particles	[μm]
	v_o	is the average depth of starting cylindrical particles	[μm]
	d	is the average sulfonated layer thickness.	[μm]

The logarithmic form of Equation 4.5 was used for the kinetics data processing:

$$\ln(-\ln(1-\alpha)) = \ln k + m \cdot \ln t \tag{4.7}$$

The linear relationship described by Equation 4.7 was plotted in Figure 4.17. The resulting overall rate constants and the exponent factors of the heterogeneous sulfonation reaction at -5°C, 22°C, 50°C, calculated from the slopes of the curves, were presented in Table 4.8.

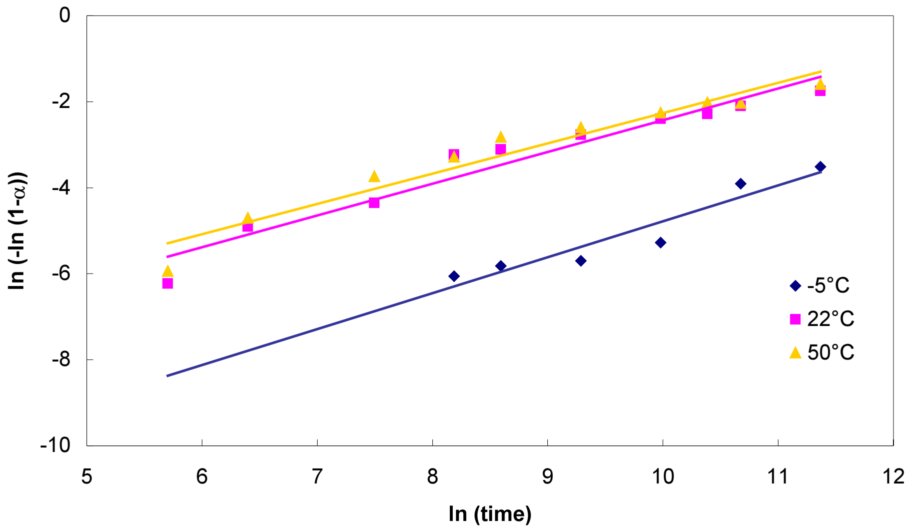


Figure 4.17 *The logarithmic linear relationship between the time and JMAJK function*

Table 4.8 *The overall rate constants and the exponent factors for sulfonation at temperature –5°C, 22°C, 50°C calculated from JMAJK equation*

T [°C]	k $[s^{-1}]$	m
-5	$1.9709 \cdot 10^{-6}$	0.8358
22	$5.5048 \cdot 10^{-5}$	0.7375
50	$9.0388 \cdot 10^{-5}$	0.7049

The values of exponent (m) ranging from 0.70 to 0.84 were approximated to the theoretical values for diffusion controlling process (0.53-0.58) [39]. The diffusion of SO_3 across a barrier of SPS to the reaction interface, at which the sulfonation is fast, was the directed step of heterogeneous sulfonation. The slight increase of the exponent m against the theory was caused by the incomplete sulfonation yield in the sulfonated layer probably due to the steric hindrance of some benzene rings. The overall rate constant (k) of heterogeneous sulfonation on solid PS surface was slightly increased with increasing temperature. The activation energy of sulfonation of PS was evaluated by means of Arrhenius equation:

$$\ln k = \ln A - \frac{E_a}{RT}, \tag{4.8}$$

where	A	is the pre-exponential factor	$[s^{-1}]$,
	E_a	is the activation energy of sulfonation reaction	$[kJ.mol^{-1}]$.

In the Figure 4.18. was depicted the linear relationship between the logarithm of rate constant, calculated from Arrhenius equation, and the inversion value of temperature plotted to estimate activation energy of sulfonation reaction.

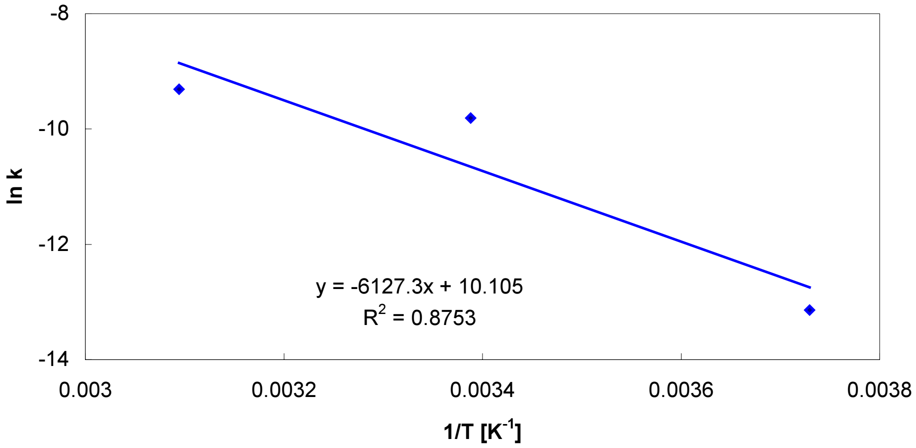


Figure 4.18 *Linear relationship between the logarithm of rate constant, calculated from Arrhenius equation, and the inversion value of temperature plotted to activation energy of sulfonation reaction*

The activation energy of heterogeneous sulfonation reaction, computed from Arrhenius equation, mentioned above, was $E_a = 50.94$ kJ.mol^{-1} and the pre-exponential factor $A = 2.45 \cdot 10^4$ s^{-1}. The activation energy of heterogeneous sulfonation using SO_3 as sulfonating agent, determined by experimental data evaluated from JMAJK equation, was equal to the activation energy of diffusion. In reason this fact, the diffusion was the main process directing yield of heterogeneous sulfonation.

4.4 Applications of SPS to modify concrete pastes

Preliminary study of polymer addition on the mechanical properties of polymer modified concrete samples was attempted. Completely water-soluble sulfonated PS and mainly surface sulfonated PS modifiers were introduced into concrete materials. First, water-soluble sulfonated PS decreased the amount of water necessary to achieve required workability of the concrete mixture. The enhancement of mechanical strength of cured cement pastes was caused by reduction of the amount of macrodefects and the absence of these macrodefects lead to preparation of high-strength concrete materials. Second, water-insoluble portion of surface sulfonated PS cannot reduce the volume of water necessary to affect workability of the concrete mixture. On the other hand mainly surface-sulfonated PS additives improve thermal insulation and decrease the density of concrete materials. The chemical interaction between the sulfonated additives and concrete particles could by probably expected. Two samples with different sulfonic groups concentration and nonsulfonated PS for comparison were prepared in this experiment. Mechanical properties of polymer-concrete samples are shown in Figures 4.19–4.20.

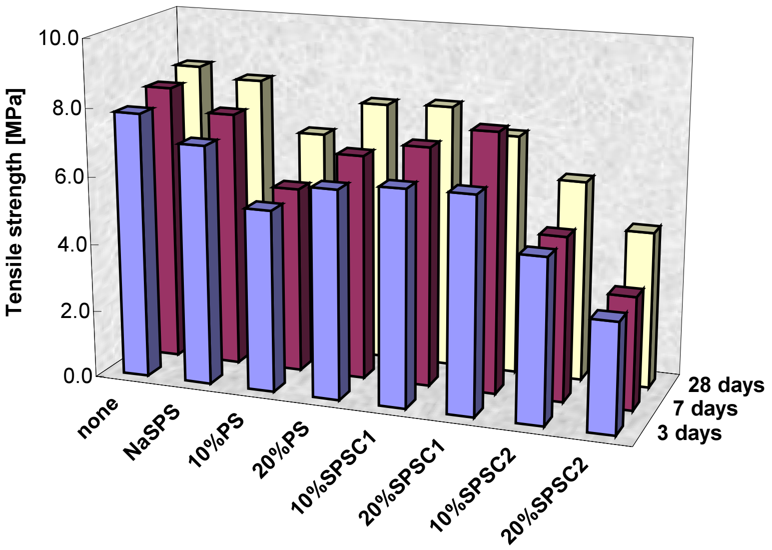


Figure 4.19 *Comparison of the tensile strength of polymer concrete samples containing addition of water-soluble NaSPS, milled foamed PS and insoluble sulfonated foamed polystyrenes SPSC1 and SPSC2 with concrete without polymeric modifier*

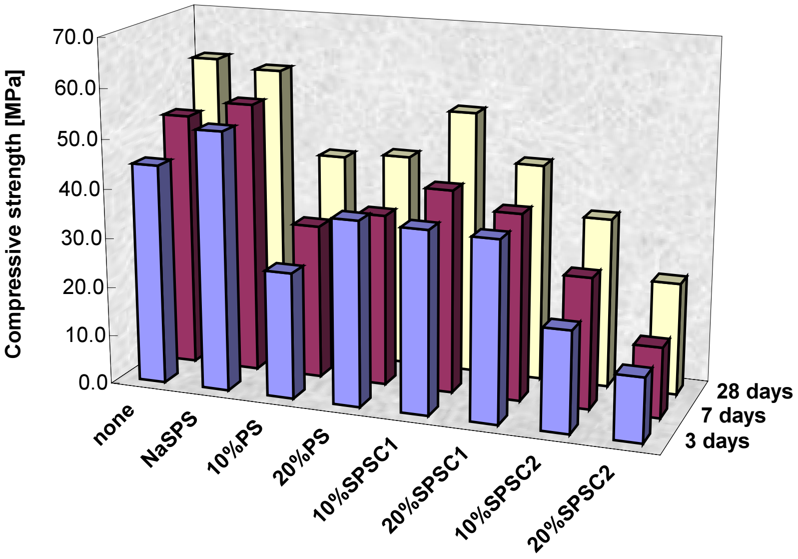


Figure 4.20 *Comparison of the compressive strength of polymer concrete samples containing addition of water-soluble NaSPS, milled foamed PS and insoluble sulfonated foamed polystyrenes SPSC1 and SPSC2 with concrete without polymeric modifier*

The comparison of mechanical properties of polymer-concrete samples, containing addition of sulfonated foamed SPSC 1, with the polymer concrete samples modified using nonsulfonated initial crushed foamed PS gave interesting results. The comprehensive strength in the case of addition SPSC 1 increased of approximately 26.6 % compare to same addition of initial foamed PS. The tensile strength of polymer-concrete sample No.1 was slightly decreased in regard to tensile strength of polymer-concrete sample modified using nonsulfonated PS. Generally, the tensile strength of polymer-concrete samples decreased in the range from 6.5 to 58.8 % in the case of addition of polymers SPSC 1 and SPSC 2. The PS addition was used to prepare reference samples to the samples containing addition of sulfonated PS. The compressive strength decreased in the case of using crushed foamed PS in the interval from 20 % to 71 %, a density of samples decreased to 89.7 %, simultaneously.

5 CONCLUSIONS

The aim of this work was to investigate mechanism and kinetics heterogeneous sulfonation of waste PS(s) with SO_3 (g). In order to gain insight into the reactions governing this process, the homogeneous sulfonation in solution was carried out first. The main goal was to achieve good understanding of the reaction mechanisms and kinetics. In order to prepare highly sulfonated, water-soluble PS by homogeneous sulfonation, the influence of acetyl sulfate concentration on the yield of sulfonation was investigated. The sulfonation yield increased approximately linearly with increasing acetyl sulfate concentration. The solubility behavior of prepared SPS, in dependence on the sulfonation level, was observed. The M_w of starting PS was the second, structural variable used in studying the affected yield of homogeneous PS sulfonation. The rate constants of homogeneous sulfonation of PS solution in DCE using acetyl sulfate were calculated to explain dependence of sulfonation rate on the M_w. Finally, the calcium salt of highly sulfonated PS by homogeneous sulfonation using acetyl sulfate in DCE solution was prepared. Based on the neutralization of SPS solution in ethanol using $CaCO_3$, new separation method of CaSPS from reaction mixture was developed and pure CaSPS was isolated.

In order to verify experimentally own hypothesis that the heterogeneous sulfonation proceeds mainly on the PS surface and, thus the surface topology will be an important structural variable, several types of PS particles with different specific surface area and different morphology were prepared. Substantially higher sulfonation rate was observed in the case of precipitated PS powder (with surface area of 33.37 $m^2.g^{-1}$) compared to the case other PS materials sulfonation (of specific surface areas ranging from 0.017 to 11.18 $m^2.g^{-1}$) which occurred with approximately identical sulfonation rate independently of their specific surface areas. This fact supports the predicted influence of the surface morphology of initial PS particles on the limiting maximum degree of sulfonation. The structure of sulfonated product was determined using FT-IR spectroscopy and elemental analysis. The determination of sulfone bridges content was attempted using ICP elemental analysis completed with alkalimetric titration, however the numeric value was not determined. On the basis of the ascertained facts and using experiences from the low molecular compound sulfonation reactions (such as sulfonation of ethylbenzene mechanism) of the heterogeneous sulfonation was determined. The sulfonation proceeds in the p-position of benzene ring and in reason of steric hindrance caused with polymeric chain and maximum one sulfonic group per one benzene ring can be attached. The rate constants of heterogeneous sulfonation of PS powders in the initial stage of reaction were determined from proposed kinetics equation of first order reaction mechanism. The presence of crosslinking of SPS prepared by heterogeneous sulfonation using SO_3 was proved by swelling of polymer particles in water instead of dissolution. The increased content of sulfone bridge with increasing temperature was estimated.

In center of attention of this work was the kinetics study of heterogeneous sulfonation reaction on the solid PS surface using SEM and EDAX measurements. The diffusion of SO_3 through the barrier of sulfonated product was the parameter determining the rate and yield of heterogeneous sulfonation. The formation of distinct sulfonated layer on PS surface was observed. The diffusion coefficients of SO_3 for three temperatures were calculated assuming validity of parabolic law and the activation energy of diffusion SO_3 into PS were determined as 49.13 $kJ.mol^{-1}$. The experimental data were fitted using JMAJK equation to obtain the overall rate constant of heterogeneous sulfonation on solid PS surface and to obtain exponent factor values from about 0.7 to 0.84, which confirmed the sulfonation as diffusion controlled process [39]. The activation energy calculated using results of JMAJK equation had value 50.94 kJ.mol^{-1}, which approximately agrees with the activation energy of diffusion.

The influence of sulfonated PS addition on mechanical properties of polymer concrete samples was studied. Although the fact that the polymer additions generally reduced the mechanical properties of concrete samples, the sulfonated foamed PS SPSC1 (with about 7.4 mole % of sulfonic groups) gave increased tensile and compressive strength compare to concrete with the same addition of nonsulfonated milled foamed PS.

6 REFERENCES

1. Nickless G., „Inorganic Sulphur Chemistry“, Elsevier, New York, p.388-405, 1968
2. Lovejoy R.W., Collwell J.H., Eggers D.F., Halsey G.D., J. Chem. Phys., Vol. 36, p. 612, 1962
3. E.E. Gilbert, Chem. Rev., Vol. 62, p. 549, 1962
4. G. Nickless, „Inorganic Sulphur Chemistry”, Elsevier, New York, p. 3884, 1968
5. Gilbert E.E., „Sulfonation and Related Reaction“, Interscience, New York, p.4, 1965
6. R.O.C. Norman and R. Taylor, Electrophilic Substitution in Benzenoid Compounds, Elsevier, Amsterdam, p. 225, 1965
7. F.A. Long and M.A. Paul, Chem. Rev., Vol. 57, p. 935, 1957
8. H. Cerfontain, „Mechanistic Aspests in Aromatic Sulfonation and Desulfonation”, Wiley, New York, p. 20 , 1968
9. O. Červinka, „Chemistry of Organic Compounds”, SNTL Alfa Prague, p.812, 1985
10. O. Červinka, V. Dědek, „Organic Chemistry”, SNTL Alfa Prague, p. 217-9, 1982
11. H. Cerfontain, „Mechanistic Aspects in Aromatic Sulfonation and Desulfonation”, Wiley, New York, p. 32, 1968
12. H. Cerfontain, A. Telder, Rec. Trav. Chim., Vol. 84, p. 1613, 1965
13. H. Cerfontain, H.J. Hofman, A. Telder, Rec. Trav. Chim., Vol. 83, p. 493, 1964
14. G.A. Ratclif, Diss. Abstracts, Vol. 14, p. 2018, 1954
15. H. Cerfontain, „Mechanistic aspect in Aromatic Sulfonation and Desulfonation“, New York, p.13, 1968
16. Krylov E.N., Chochlova C.G., Zhur. Obshchej. Chim., Vol. 52(2), p.390-393, 1981
17. W. Breuers, H. Mark, E. Konrad, US 2,031,929, 1936
18. C. Wulf, Ger. 580,366 (1933), Brit. 367,416, 1933
19. A.F. Turbak, Ind. Eng. Chem., Prod. Res. Dev., Vol. 1(4), p. 275, 1962
20. Makowski et. al., USP 3,870,841, 11.3.1975
21. R.A. Weiss, Ashish Sen, C.L. Willis, L.A. Pottick, Polymer, Vol. 32(10), p. 1867, 1991
22. C.W. Plummer et.al., „Development of sulfonated PPO for Reverse Osmosis”, OSW Research and Development Report, Vol. 551, 1970
23. P.J. Chlodzinski, A.P. Fickett, A.B. Laconti, Polym. Prepr., Vol. 12(2), p. 276, 1971
24. R.Y.M Huang, J.J. Kim, J. Appl. Pol. Sci., Vol. 29, p. 4017, 1984
25. W.A. Thaler, J. Pol. Sci., Pol. Chem. Ed., Vol. 20, p. 875, 1982
26. W.A. Thaler, C. du Brevil, J. Pol. Sci., Pol. Chem. Ed., Vol. 22, p. 3905, 1984

27. B. Siadat, R.D. Lundberg, Pol. Eng. and Sci., Vol. 20(8), p. 530, 1980
28. K. Jin, M.T. Bishop, T.S. Ellis, F.E. Karasz, Br. Polym. J., Vol. 17, p. 4, 1985
29. Z.L. Zhou, A. Eisenberg, J. Pol. Sci., Pol. Phys. Ed., Vol. 27, p. 657, 1982
30. D. Rahrig, W.J. MacKnigt, R.W. Lenz, Macromolecules, Vol. 12, p. 195, 1979
31. H. Vink,. Macromol Chem., Vol. 182, p. 279, 1981
32. W.A. Thaler, Macromolecules, Vol. 16, p. 623, 1983
33. G.Y. Kim, R. Salovey and J.J. Aklonis, Pol. Bulletin, Vol. 23, p. 543, 1990
34. F.P. Regas, Polymer, Vol. 25, p. 249, 1984
35. W.R. Carrol and H. Eisenberg, J. Pol. Sci., Part A-2, Vol. 4, p. 599, 1966
36. M.T. Bishop, F.E. Karazs, P.S. Russo, K.H.Langley, Macromolecules, Vol. 18, p. 86, 1985
37. W.J. Moore, „Fyzikální chemie", SNTL Praha, p.377, 1979
38. E.Erdös, M. Kubín, „Malé Makromolekulární monografie", ÚMCH ČSAV, Praha, Vol. 14, p. 49, 1976
39. C.H. Bamford, C.F.H. Tipper, Comprehensive Chemical Kinetics, Elsevier Scientific Publishing Comp., Amsterdam, Vol. 22, p.41-113, 1980

Abstract

The current knowledge of polystyrene (PS) sulfonation was reviewed. The experimental part of this work was focused on preparation of the water-soluble PS. The kinetic parameters of both homogeneous and heterogeneous sulfonation were studied. The main attention was focused on the study of heterogeneous sulfonation of solid PS using gaseous SO_3 diluted with air. The influence of temperature, M_w of starting PS, specific surface area of solid PS particles and their morphology on the mechanism and kinetics of heterogeneous sulfonation were investigated. The sulfonated PS samples were characterized using elemental ICP analysis, alkalimetric titration, EDAX microanalysis, FT-IR spectroscopy and SEM measurement. The preliminary application of surface sulfonated foamed PS and water-soluble sodium salt of polystyrenesulfonic acid to concrete samples was attempted.

Český abstrakt

Práce shrnuje současné poznatky v oblasti sulfonace polystyrenu (PS). Experimentální část je zaměřena na přípravu sulfonovaného PS rozpustného ve vodě. Byly určeny kinetické parametry homogenní i heterogenní sulfonace. Zvláštní pozornost je věnována studiu mechanismu heterogenní sulfonace PS částic plynným oxidem sírovým ve směsi se vzduchem. Byl sledován vliv teploty, molekulové hmotnosti (M_w) výchozího PS, vliv specifického povrchu a morfologie povrchu PS částic PS na mechanismus a kinetiku heterogenní sulfonace. Připravené vzorky sulfonovaných PS byly charakterizovány elementární ICP analýzou, alkalimetrickou titrací, FT-IR spektroskopií, skenovací elektronovou mikroskopií a EDAX mikroanalýzou. Byla testována možnost aplikace povrchově sulfonovaných částic PS a ve vodě rozpustné sodné soli polystyrensulfonové kyseliny do betonů.

CURRICULUM VITAE

Surname: Kučera
Name: František
Title: Mgr.
Date of birth: 26.3.1970
Place of birth: Brno
Nationality: Czech

EDUCATION:

Master Study: (1988-1994)
Masaryk University Brno
Faculty of Science
Department of Inorganic Chemistry
Kotlařská 2, 602 00 Brno, CZ
Major Advisor: Doc. RNDr. J. Příhoda, CSc.
Thesis Topic: Nucleophilic Substitution of Dichloride of Trichloromethylthiophosphoric(V) Acid Using Amines

Postgraduate Study: (1994-2001)
Technical University of Brno
Faculty of Chemistry
Institute of Material Chemistry
Department of Macromolecular Chemistry
Purkyňova 118, 612 00 Brno, CZ
Major Advisor: Prof. RNDr J. Jančář, CSc.
Thesis Topic: Homogeneous and Heterogeneous Sulfonation of Polystyrene

PUBLICATIONS:

[1] Kučera F., Jančář J.: Preliminary Study of Sulfonation of Polystyrene by Homogeneous and Heterogeneous Reaction, *Chem. Papers*, 50(4), 1996, p. 224-228, ISSN 0366-6352
[2] Kučera F., Jančář J.:Sulfonation of Polystyrene, International Conference of PhD Students, University of Miskolc, Hungary, August 11-17, 1997, Engineering science I., p. 275-276
[3] Kučera F., Jančář J.: Homogeneous and Heterogeneous Sulfonation of Polymers: A Review, *Polym. Eng. Sci.*, 38/5, 1998, p. 783-792, ISSN 0032-3888
[4] Fišera M., Kučera F.: Determination of Sulphuric by ICP-OES for Preliminary Study of Sulfonation of Polystyrene by Homogeneous and Heterogeneous Reactions, *Fresenius J. of Anal. Chem.*, 1998– in press, ISSN 0937-0633