Colloid Polym Sci 277:579–582 (1999)

SHORT COMMUNICATION

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Microanalysis of the surface concentration of sulfate groups at polystyrene particle by isothermal titration calorimetry

Received: 15 December 1998
Accepted in revised form: 24 February 1999

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Part CXC of the series "Studies on Suspension and Emulsion"

Abstract Microanalysis of sulfate groups at polystyrene particle surfaces, which were derived as persulfate initiator fragments, was carried out with isothermal titration calorimetry, and compared with a conventional conductometric titration. The quantitative analysis was possible even with an extremely small number of polystyrene particles have 10 μmol sulfate groups.

Key words Isothermal titration calorimetry – Sulfate group – Polystyrene – Particle – Emulsifier-free – Emulsion polymerization

Introduction

Recently, sub-micron-sized polymer particles having functional groups such as sulfate [1, 2], carboxyl [2, 3] and amino [4] groups, produced by emulsion polymerization have been applied in the biomedical field, microelectronics, etc. Especially functional groups at polymer particle surfaces are useful for these applications.

The conductometric titration (CT) method is one of the traditional determination methods for ionic groups at particle surfaces; however, the method needs a large amount of sample to get an accurate value [5]. Since it is often difficult to use a large amount of a valuable particle, appropriate microanalysis is required.

In the biochemical field, various kinds of heat-analysis methods are used for microanalysis of any reaction; one of these methods is isothermal titration calorimetry (ITC). This method has the potential advantage that a quantitative analysis can be done even with an extremely small amount of sample.

In this article, the number of sulfate groups at polystyrene (PS) particle surfaces produced by emulsifier-free emulsion polymerization with potassium persulfate as initiator will be estimated by ITC.

Experimental

Materials

Styrene was purified by distillation under reduced pressure in a nitrogen atmosphere. Potassium persulfate was purified by recrystallization. Deionized water with a specific conductivity of $5 \times 10^6\ \Omega$ cm was distilled. Potassium hydroxide and potassium hydrogen sulfate were used as received (nakarai tesk). The cation-exchange resin (Amberlite, IR-120B, Organo Co.) was treated with 1 N HCl to change it to the protonated form.

Preparation of PS emulsions

PS particles having different numbers of sulfate groups at their surfaces were produced by emulsifier-free emulsion polymerization carried out under the conditions listed in Table 1 in a three-neck round-bottom flask equipped with a Teflon paddle stirrer operating at 240 rpm. The PS emulsions obtained were purified by ultracentrifuging washes with distilled water 5 times, and ion exchange. Finally the solid content was adjusted to 2–20 wt% for ITC or CT measurements.

Measurement of the heat of the neutralization reaction by ITC

The measurement of the heat of the neutralization reaction between sulfate groups and KOH was carried out with by ITC (CSC Co., model 4200 ITC). The calorimeter was controlled by computer, except for changing titrant and titrate.

The sample and reference cells filled with 1 ml $KHSO_4$ aqueous solution or PS emulsion were set into the calorimeter and were maintained at 25 °C for several hours. A long needle microsyringe with 0.05 N KOH was set on the calorimeter and put for 15–20 min. All measurements were carried out under the conditions listed in Table 2. All results are given as the mean of three measurements.

Determination of sulfate groups by CT

CT was carried out at room temperature with 20 g PS emulsion and 0.005 N KOH using an autotitrator (Hiranuma sangyo Co., RAT-II). One drop of the titrant was 0.1 ml and the conductance of the system was measured after standing for 20 s.

Results and discussion

The evolution of heat at the five additions of 25 μl 0.05 N KOH every 200 s in 1 ml 0.2 mM $KHSO_4$ aqueous solution (curve a) and in distilled water (curve b), measured by ITC at 25 °C, is shown in Fig. 1. The heat evolution depicted by curve a includes the heats of mixing and dilution in addition to that of the neutralization reaction. The heats of mixing and dilution should be estimated from the heat evolution depicted by curve b. The peak area of the first peak of curve a exceeded that of curve b, and the other peaks were almost the same. This indicates that upon the first addition of KOH to the $KHSO_4$ aqueous solution, the neutralization reaction was completely over. Therefore, the heat of the neutralization reaction can be obtained by subtraction of the heat evolved upon the first addition (i.e. curve a minus curve b). In the curve b, the peak area decreased with an increase in the frequency of KOH addition because of the difference in KOH concentration between the titrate and the titrant (0.05 N). That the first peak area was the biggest due to addition of KOH to distilled water seems not to be based on mixing but on dilution.

The relationship between the concentration of $KHSO_4$ aqueous solution and the heat of the neutralization reaction is shown in Fig. 2: a linear relationship was established. In the homogeneous system, the determination of the number of sulfate groups was possible even with 10 μmol $KHSO_4$. The heat of the neutralization reaction per mole of KOH calculated from this relationship was 51 kJ. This value agrees well with the 54–56 kJ/mol for the heat of the neutralization reaction of strong acids with strong bases [6].

Table 1 Recipes of emulsifier-free emulsion polymerizations for the preparation of polystyrene particles having various concentrations of sulfate groups at the surface[a]

Ingredients		no. 1	no. 2
Styrene	(g)	60	60
Potassium persulfate	(g)	1.32	0.44
Water	(g)	2000	2000
Dh[b]	(nm)	370	397
ζ-potential	(mV)	−30	−17

[a] N_2; 70 °C; 48 h; stirring rate, 120 rpm

[b] Hydrodynamic diameter measured by dynamic light scattering

Table 2 The titration conditions for sulfate groups with KOH by isothermal titration calorimetry

Titrant molarity[a]	(mol/l)	0.05
Injection volume	(μl)	25
Number of injections		5
Titrate molairty[b]	(mol/l)	$> 5 \times 10^{-3}$
Titrate volume in cell	(ml)	1
First injection time	(s)	200
Time between injections	(s)	200
Temperature[c]	(°C)	25.0
Stirrer	(rpm)	100

[a] Using KOH aqueous solution

[b] Molarity which reacted completely with an injection of KOH

[c] Controlled by very stabile bath (±0.0005 °C)

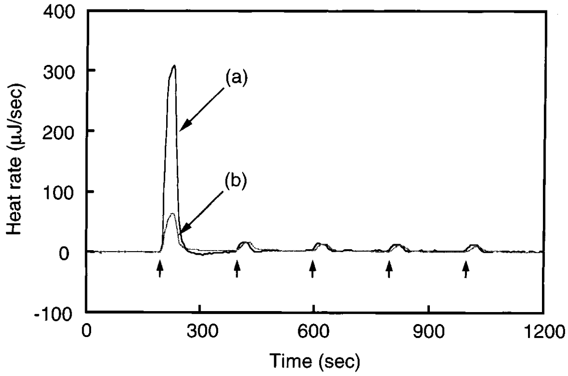

Fig. 1 Titration charts 1 ml 0.2 mM $KHSO_4$ aqueous solution (*a*) and distilled water (*b*) with 0.05 N KOH (25 μl) 5 times using isothermal titration calorimetry under the titration conditions listed in Table 2

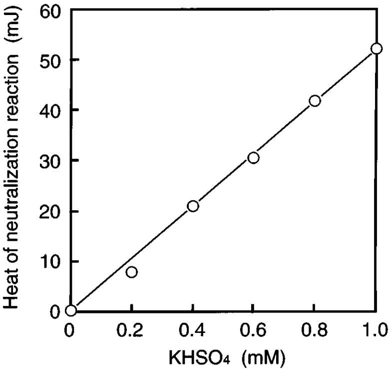

Fig. 2 Relationship between the concentration of $KHSO_4$ aqueous solution (1 ml) and the heat of the neutralization reaction generated with 0.05 N KOH (125 μl)

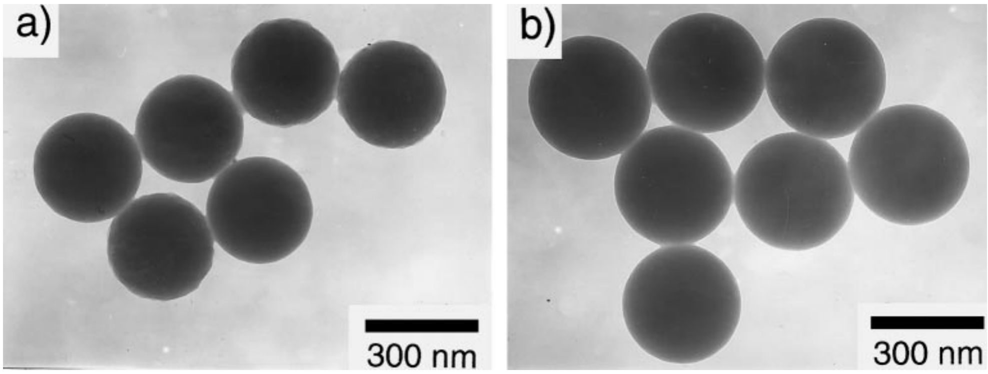

Fig. 3a, b Transmission electron microscopy photographs of polystyrene (*PS*) particles produced by emulsifier-free emulsion polymerization under the conditions listed in Table 1

Figure 3 shows transmission electron microscopy photographs of two kinds of PS particles having different numbers of sulfate groups at their surfaces produced by emulsifier-free emulsion polymerization under the conditions listed in Table 1. These PS particles have similar diameters and different ζ-potential values. There are some reports showing that almost all of the sulfate groups derived as persulfate initiator fragments are localized at particle surfaces [7]. The PS emulsions obtained were mixed with the protonated form of the cation-exchange resin for 5 h to change -SO$_4$K to -SO$_4$H after purification by ultracentrifuging with distilled water for the ITC measurements.

Typical titration charts of 1 ml PS emulsion (solid content: 1 wt%) (curve a) and of distilled water (curve b) with 125 μl 0.05 N KOH at 25 °C using ITC are shown in Fig. 4. As for the homogeneous system shown in Fig. 1, the first peak of the curve a was larger than that of curve b and did not have a tail. The other peaks were also almost the same in both curves. This indicates that the neutralization reaction of sulfate groups at the PS particle surfaces was completed within 100 s. Because PS is a hydrophobic polymer and its glass-transition temperature is much higher than the titration temperature of 25 °C, it should take considerable time for KOH to penetrate into the inside of the PS particles. This indicates that in the first titration shown by curve a, all the sulfate groups at the PS particle surfaces are titrated and the sulfate groups inside the PS particles are not titrated even if they exist there.

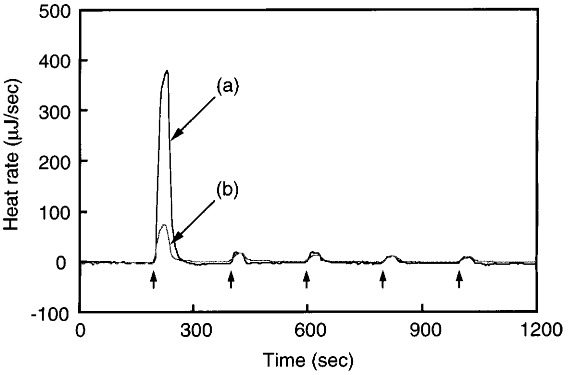

Fig. 4 Titration charts of 1 ml 1 wt% PS emulsion (no. 1) (*a*) and distilled water (*b*) with 0.05 N KOH (125 μl) using isothermal titration calorimetry under the titration conditions listed in Table 2

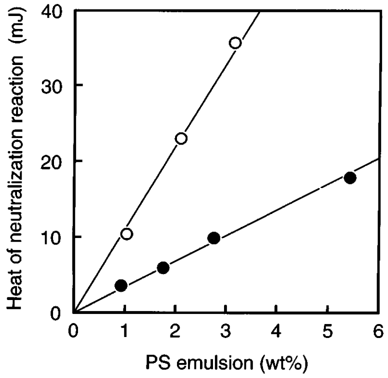

Fig. 5 Relationships between the solid content of PS emulsions (1 ml) and the heat of the neutralization reaction with 0.05 N KOH (125 μl) at 25 °C. The PS emulsions were prepared under the conditions listed in Table 1: ζ-potential (mV): ○, -30 (no. 1); ●, -17 (no. 2)

The relationships between the solid contents of the two kinds of PS emulsions and the heat of the neutralization reactions are shown in Fig. 5. In both cases, linear relationships were established. In the system of no. 1 PS particles which have more sulfate groups at the surfaces, the heat of the neutralization reaction per gram of particles was larger than that of the no. 2 PS particles. These results indicate that quantitative analysis for sulfate groups at the PS particle surfaces with ITC is possible. The number of sulfate groups at the PS particle surfaces was obtained using the linear relationship between the KHSO$_4$ concentration and the heat of neutralization shown in Fig. 2.

The relationships between the number of no. 1 PS particles used in the ITC and (CT) measurements and the numbers of sulfate groups estimated by both

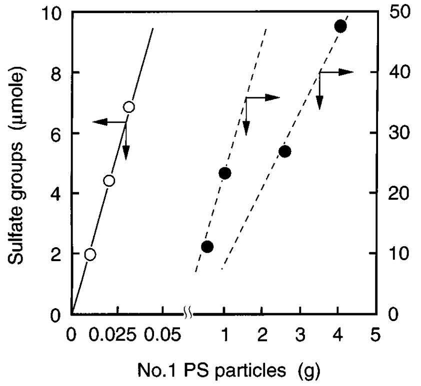

Fig. 6 Relationships between the number of PS particles (no. 1) for measurements and the total numbers of sulfate groups at the PS surfaces estimated by isothermal titration calorimetry (○) and conductometric titration (●)

titrations are shown in Fig. 6. In CT, the data obtained for PS amounts less than 4 g were scattered in the range 0.78–1.36 μmol/m^2. On the other hand, ITC gave reliable results of 1.75 μmol/m^2 even at amounts less than 0.03 g. As expected from Fig. 5, a reliable number for the sulfate groups of the no. 2 PS particles was also obtained (0.48 μmol/m^2) by ITC with the same low PS amounts. However, the data obtained by CT with 4 g were not reliable because of the smaller number of sulfate groups for the no. 1 PS particles.

From the above results, it is concluded that the estimation of sulfate groups as initiator fragments at PS particle surfaces by ITC is possible even with an extremely small amount of sample.

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