

Catalytic Activity of Poly(α -sulfoundecenoic acid)

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(Received January 17, 1992)

ABSTRACT: Poly(α -sulfoundecenoic acid), poly(SUA-H), was prepared from poly(undecenoic acid), poly(UA-H). The critical micelle concentration, CMC, and pre-CMC of poly(SUA-H), estimated with measurement of electric conductivity of the aqueous solution, were slightly higher than those of poly(sodium undecenoate), poly(UA-Na), and benzene was solubilized into aqueous solution of poly(SUA-H) at the concentrations above the pre-CMC. Catalytic activity of poly(SUA-H) on the acid hydrolyses of sucrose and *p*-nitrophenyl acetate, PNPA, was examined. For the hydrolysis of sucrose in water, the catalytic activity of poly(SUA-H) was slightly lower than that of hydrochloric acid and the catalysis followed an ordinary second-order kinetics. For the hydrolysis of PNPA in ethanol–water mixture (1 : 1 in vol.), the catalytic activity was slightly higher than that of hydrochloric acid, although the catalysis seemed to follow an ordinary second-order kinetics. For the hydrolysis of PNPA in water, however, catalytic activity was found to be considerably higher than those of hydrochloric acid and low molecular weight analog of poly(SUA-H). The reaction rate showed a saturation phenomenon with increasing concentration of poly(SUA-H), although it increased proportionally with increasing concentration of PNPA in the examined range. Lineweaver–Burk plots of the kinetic data showed good straight lines, which indicated that the catalysis followed a Michaelis–Menten type kinetics. These results can be explained by hydrophobic interactions of the catalyst with the substrate.

KEY WORDS Catalytic Activity / Poly(α -sulfoundecenoic acid) / *p*-Nitrophenyl Acetate / Hydrophobic Interaction / Hydrolysis / Michaelis–Menten type Kinetics / Lineweaver–Burk Plot /

Sodium 10-undecenoate[CH₂=CH-(CH₂)₈-COONa], UA-Na, has been found to form micelles at concentrations higher than its pre-critical micelle concentration, pre-CMC, and to polymerize effectively in the micelle form under irradiation with UV light¹ or γ -ray.^{2–5} The obtained polymer was found to have some interesting characteristics such as a more intensively hydrophobic domain than that of the monomeric counterpart in water.⁶ We have investigated catalysis systems in the presence of poly(UA-Na) derivatives. In the present paper we report the catalytic activity of poly(α -sulfoundecenoic acid) ($[-\text{CH}_2-\text{CH}(\text{CH}_2)_7-\text{CH}(\text{COOH})(\text{SO}_3\text{H})-]_n$), poly(SUA-H), which has been prepared from poly(UA-Na), on acid hydrolyses of sucrose and

p-nitrophenyl acetate, PNPA.

EXPERIMENTAL

Reagents

PNPA was purified by recrystallization from ethanol. Water was deionized and distilled. All other commercially available reagent grade chemicals were used without further purification.

Preparation of Poly(SUA-H)

Poly(UA-Na) was obtained by polymerization of UANa (0.1 mol l⁻¹ aqueous solution) by irradiation with UV light for 24 h at 60°C according to the method previously reported.¹ Yield and number-average degree of po-

lymerization were about 12% and 12, respectively. The polymer was acidified with 0.1 mol l^{-1} hydrochloric acid, dried in vacuum, extracted with tetrahydrofuran, and then dried in vacuum. The obtained acid-form polymer was dissolved in dimethylformamide and sulfonated with sulfur trioxide according to the method reported by Weil, *et al.*⁷ to obtain poly(SUA-H). The polymer was stored as the sodium salt and the salt was converted to free acid form by means of an ion exchange column just before use.

Sulfuric acid group content of the polymer was determined by elemental analysis and titration with aqueous solution of sodium hydroxide. Although there was a little difference between the obtained values of the sulfonic acid group content, the values obtained by the titration was used for calculation of catalyst concentration in the catalysis.

Estimation of CMC and Pre-CMC of Poly(SUA-H) Aqueous Solution

Electric conductivity of various concentrations of poly(SUA-H) was measured using a conductometer (Toa Electric Co., Tokyo: CM-40M) and CMC and pre-CMC were estimated from the break points of the plot of the electric conductivity against the concentration.

Estimation of the Maximum Amount of Solubilized Benzene

Benzene was added dropwise from a microburet into aqueous solution of poly(SUA-H) and the amount of benzene just before turbidity appeared, monitored with a turbidimeter, was estimated as the maximum amount of solubilized benzene.

Measurement of Hydrolysis Rates

For the hydrolysis of sucrose, a given amount of the catalyst polymer was dissolved in water and added to a sucrose aqueous solution. The resulting mixture was kept at 25°C and aliquots of the mixture were taken

out at intervals, and the optical rotatory powers were measured by a polarimeter (Atago Seisakusho, Tokyo: Polax). The hydrolysis rates were calculated as initial rates of the reaction. For hydrolysis of PNPA, the catalyst polymer was dissolved in ethanol-water mixture (1:1 in vol.) or in water and solid PNPA was added directly to the solution in a quartz cell for measurement of UV light absorption just before measurement. The reaction mixture was kept at 25°C and the increase in absorption at 317 nm, which was assigned to nitrophenol, was followed continuously with reaction time. The catalytic reaction rate was calculated as difference in the apparent and spontaneous reaction rates; the latter was determined as the reaction rate in the absence of the catalyst.

IR Absorption Spectrum

IR absorption spectra of sodium salt of poly(SUA-H) and UANa were obtained by a double beam grating spectrometer (Hitachi Seisakusho Co., Tokyo; Hitachi EPG-3) applying the KBr disk technique.

RESULTS

Figure 1 shows the IR absorption spectrum of sodium salt of the prepared poly(SUA-H), poly(SUA-Na), together with that of UANa. In the spectrum of poly(SUA-Na), absorption peaks assigned to sulfonate group at 1130 and 970 cm^{-1} are found, and those related to the double bond at 3080, 1640, 990, and 910 cm^{-1} , found in the spectrum of UANa, are not found.

The electric conductivity of aqueous solutions of poly(SUA-H) was measured. Figure 2 shows a plot of the electric conductivity against the concentration of poly(SUA-H) with sulfonic acid group content of 29 mol% (based on mole of undecenoic acid monomer unit), where the concentration of poly(SUA-H) refers to that of hydronium ion. Two break points are found at about 1.5×10^{-4} and

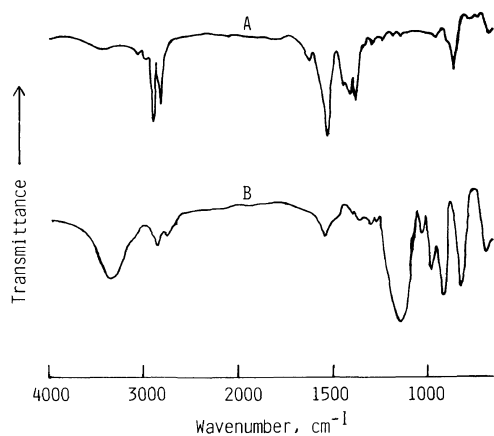


Figure 1. IR absorption spectra of sodium salt of poly(SUA-H) (B) and UANa (A). Degree of sulfonation of poly(SUA-H), 29 mol% based on undecenoic acid repeating unit.

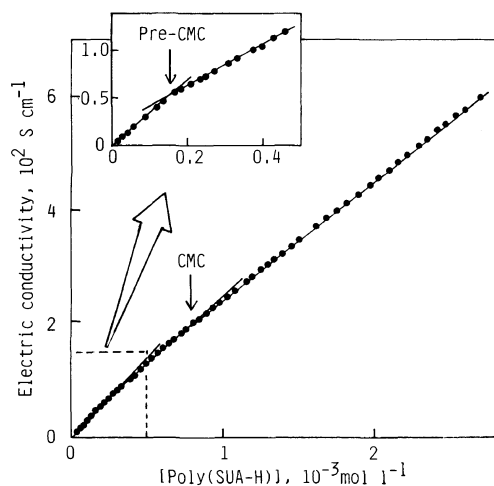


Figure 2. Plot of electric conductivity of aqueous solution of poly(SUA-H) against concentration. Degree of sulfonation of poly(SUA-H), 29 mol%. Concentration of poly(SUA-H) refers to that of hydronium ion.

$7.7 \times 10^{-4} \text{ mol l}^{-1}$, which correspond to 5.3×10^{-4} and $26.6 \times 10^{-4} \text{ mol l}^{-1}$ based on mole of undecenoic acid monomer unit, and the concentrations corresponding to the break points are estimated as pre-CMC and CMC of the poly(SUA-H), respectively. The same measurement was also carried out for poly(SUA-H) with sulfonic acid group content of

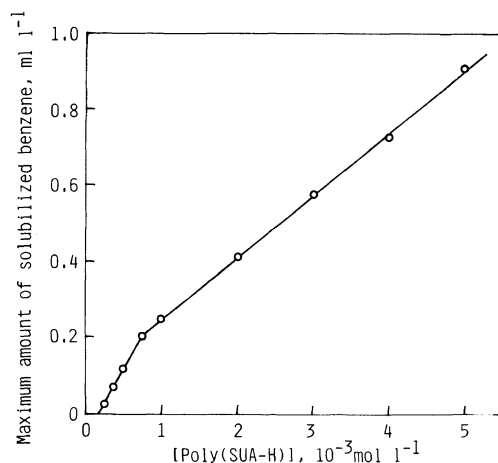


Figure 3. Plot of maximum amount of benzene solubilized into aqueous solution of poly(SUA-H) with degree of sulfonation of 29 mol%.

9 mol% and pre-CMC and CMC were found to be 0.4×10^{-4} and $1.9 \times 10^{-4} \text{ mol l}^{-1}$, which correspond to 4.4×10^{-4} and $21.1 \times 10^{-4} \text{ mol l}^{-1}$ based on mole of undecenoic acid monomer unit, respectively. These values suggest that the poly(SUA-H) molecule forms a intensively hydrophobic domain similarly to poly(UA-Na), although they are slightly higher than those of poly(UA-Na) (4.0×10^{-4} and $7.0 \times 10^{-4} \text{ mol l}^{-1}$, respectively); poly(undecenoic acid), poly(UA-H), is insoluble in water and sulfonated undecenoic acid (sulfonic acid group content 100 mol%), SUA-H, shows practically no break point in the similar plot.

Solubilization of benzene into poly(SUA-H) aqueous solution was examined. Figure 3 shows a plot of the maximum amount of solubilized benzene against the concentration of poly(SUA-H) with sulfonic acid group content of 29 mol%. The plot is composed of two straight lines and the concentrations corresponding to the start of solubilization and break point agree well with pre-CMC and CMC, respectively, estimated from measurement of electric conductivity of the aqueous solution. In the similar plot for poly(SUA-H) with sulfonic acid group content of 9 mol%,

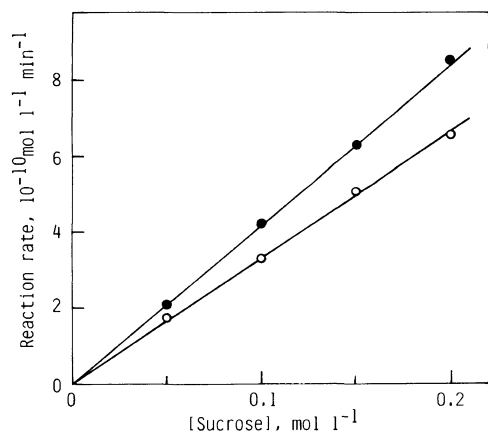


Figure 4. Plots of catalytic reaction rate against concentration of sucrose for hydrolysis of sucrose in water in the presence of poly(SUA-H) with degree of sulfonation of 29 mol% (○) or hydrochloric acid (●), at 25°C. [Catalyst], $1.0 \times 10^{-3} \text{ mol l}^{-1}$. Concentration of the catalyst refers to that of hydronium ions.

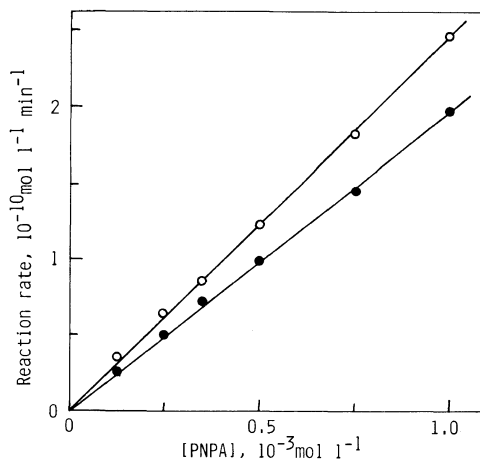


Figure 6. Plots of catalytic reaction rate against concentration of PNPA for hydrolysis of PNPA in ethanol-water mixture (1:1 in vol.) in the presence of poly(SUA-H) with degree of sulfonation of 29 mol% (○) or hydrochloric acid (●), at 25°C. [Catalyst], $1.0 \times 10^{-3} \text{ mol l}^{-1}$.

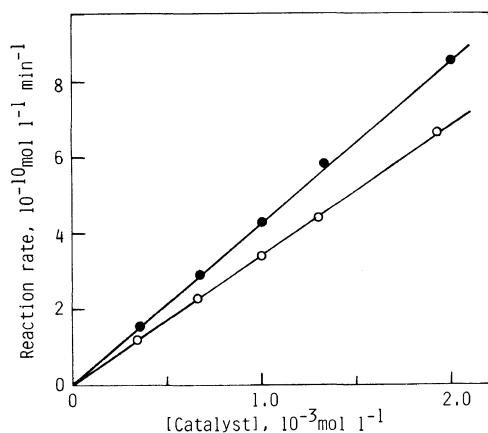


Figure 5. Plots of catalytic reaction rate against concentration of catalyst for hydrolysis of sucrose in water in the presence of poly(SUA-H) with degree of sulfonation of 29 mol% (○) or hydrochloric acid (●). [Sucrose], 0.10 mol l^{-1} .

similar tendency was found, although the maximum amount of solubilized benzene at the same concentration based on the undecenoic acid monomer unit was slightly higher than that of poly(SUA-H) with sulfonic acid group content of 29 mol%. These results indicate that hydrophobic substances can be solubilized into water in the presence of

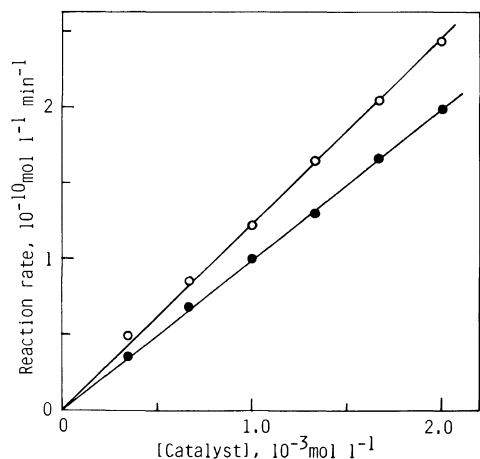


Figure 7. Plots of catalytic reaction rate against concentration of catalyst for hydrolysis of PNPA in ethanol-water mixture (1:1 in vol.) in the presence of poly(SUA-H) with degree of sulfonation of 29 mol% (○) or hydrochloric acid (●). [PNPA], $5.0 \times 10^{-4} \text{ mol l}^{-1}$.

appropriate concentration of poly(SUA-H).

Catalytic activity of poly(SUA-H) on the hydrolysis of sucrose in water was examined and compared with that of hydrochloric acid. Figures 4 and 5 show plots of the catalytic reaction rate in the presence of poly(SUA-H)

with degree of sulfonation of 29 mol% or hydrochloric acid against concentrations of the substrate and the catalyst, respectively, where the concentration of the catalyst refers to that of hydronium ion. Both the catalyses in the presence of the poly(SUA-H) and hydrochloric acid are first-order with respect to the concentrations of substrate and catalyst, and that the catalytic activity of poly(SUA-H) is about 80% that of hydrochloric acid.

Catalytic activity of poly(SUA-H) on the hydrolysis of PNPA in water-ethanol mixture (1:1 in vol.) was examined. Figures 6 and 7 show plots of the catalytic reaction rate in the presence of poly(SUA-H) with degree of sulfonation of 29 mol% or hydrochloric acid against the concentrations of the substrate and catalyst, respectively. It is found that, similar to the case of sucrose, both catalyses seem to be first-order with respect to the concentrations of the substrate and catalyst, although the catalytic activity of the poly(SUA-H) is about 10% higher than that of hydrochloric acid.

The catalytic activity of poly(SUA-H) on the hydrolysis of PNPA in water was examined. Figure 8 shows plots of the catalytic reaction rate in the presence of poly(SUA-H) with degree of sulfonation of 29 mol% or hydrochloric acid against the concentration of the substrate. In this case, the catalytic activity of the poly(SUA-H) is considerably higher than that of hydrochloric acid, although the catalysis seems to be first-order with respect to the concentration of the substrate, at least in the range examined. Figure 9 shows plots of the catalytic reaction rates in the presence of poly(SUA-H)s with sulfonation of 9 and 29 mol%, SUA-H, and hydrochloric acid as the catalyst, against the concentration of the catalyst. Poly(SUA-H)s show considerably higher catalytic activities than monomeric SUA-H and hydrochloric acid, and the catalytic reaction in the presence of poly(SUA-H)s shows a rate-saturation

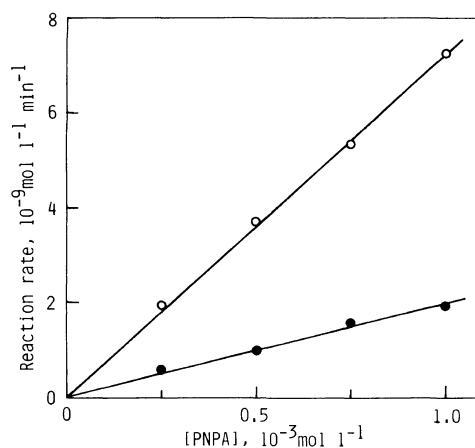


Figure 8. Plots of catalytic reaction rate against concentration of PNPA for hydrolysis of PNPA in water in the presence of poly(SUA-H) with degree of sulfonation of 29 mol% (O) or hydrochloric acid (●), at 25°C. [catalyst], $5.0 \times 10^{-4} \text{ mol l}^{-1}$.

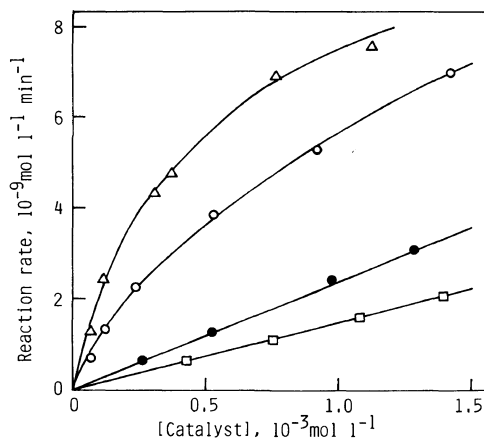
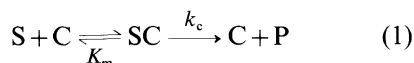


Figure 9. Plots of catalytic reaction rate against concentration of catalyst for hydrolysis of PNPA in water in the presence of poly(SUA-H)s with degree of sulfonation of 29 mol% (O) or 9 mol% (Δ), hydrochloric acid (●), or sulfonated undecenoic acid (\square). [PNPA], $5.0 \times 10^{-4} \text{ mol l}^{-1}$.

phenomenon with increasing concentration of poly(SUA-H). Poly(SUA-H) with sulfonation of 9 mol% shows a higher catalytic activity than that with sulfonation of 29 mol%. The rate-saturation phenomenon is usually found for Michaelis-Menten type reactions like enzymatic ones, although in the present case

the saturation phenomenon is just the inverse with respect to the concentrations of the substrate and catalyst. If the reaction proceeds *via* complex formation between the catalyst and the substrate, the elementary reaction can be described in the most simplified form as follows;



where S, C, SC, and P are substrate, catalyst, complex, and product, respectively. K_m and k_c are the Michaelis and rate constants, respectively. Thus, when the concentration of the catalyst is considerably higher than that of the substrate, the catalytic reaction rate, v_{cat} , is described as follows:

$$v_{cat} = (k_c [C_0] [S_0]) / (K_m + [C_0]) \quad (2)$$

where $[C_0]$ and $[S_0]$ are the initial concentrations of the catalyst and substrate, respectively. If these assumptions are valid, linear relationships must be obtained in the plots of the reciprocal reaction rate *versus* the reciprocal initial concentration of the catalyst, as in Lineweaver–Burk plot. In practice, as seen in Figure 10, the corresponding plots of the data shown in Figure 9 give rather good straight lines. Therefore, the reaction in the presence of poly(SUA-H) may be concluded to proceed kinetically *via* complex formation between the catalyst and substrate.

The kinetic parameters of these reactions were calculated from the straight lines obtained in Figure 10 and summarized in Table I. The values of K_m are found to be in the order of $10^{-4} \text{ mol l}^{-1}$. The value for poly(SUA-H) with sulfonation of 9 mol% is smaller than that with sulfonation of 29 mol%, indicating that more hydrophobic catalyst binds to the substrate more effectively. The k_c is also smaller for poly(SUA-H) with sulfonation of 9 mol% than for that with sulfonation of 29 mol%, which may indicate that substrate-binding makes the substrate stable, as often seen in the catalysis systems in the

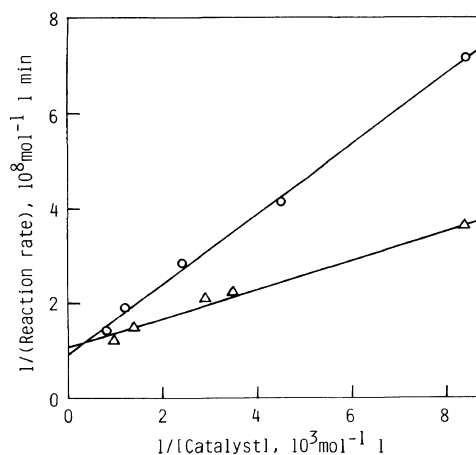


Figure 10. Lineweaver–Burk plots of the data shown in Figure 9.

Table I. Parameters of Michaelis–Menten type kinetics of hydrolysis of PNPA in water in the presence of poly(SUA-H), at 25°C

Catalyst	Poly-(SUA-H)	Poly-(SUA-H)	Sulfonated undecenoic acid	Hydrochloric acid
Degree of sulfonation/%	9	29	100	—
$K_m / 10^{-4} \text{ mol l}^{-1}$	2.9	8.3	—	—
$k_c / 10^{-5} \text{ min}^{-1}$	1.85	2.17	—	—
$k_c \cdot K_m^{-1} / \text{mol}^{-1} \text{ l min}^{-1}$	0.063	0.026	—	—
$k_2 / \text{mol}^{-1} \text{ l min}^{-1}$	—	—	0.0031	0.0049

presence of a synthetic polymer catalyst. The ratio of $k_c \cdot K_m^{-1}$ to the second-order rate constant, k_2 , of the reaction in the presence of hydrochloric acid can be considered an indication of the rate acceleration. The ratios are found to be about 13 for poly(SUA-H) with sulfonation of 9 mol% and 5 for sulfonation of 29 mol%, respectively.

DISCUSSION

From the above results, it was found that

poly(SUA-H) showed a higher catalytic activity than hydrochloric acid and monomeric SUA-H for the hydrolysis of PNPA in water and that the reaction followed a Michaelis-Menten type kinetics, although poly(SUA-H) showed an ordinary second-order catalytic behavior for the hydrolyses of PNPA in less hydrophilic water-ethanol mixture (1:1 in vol.) and of sucrose as a hydrophilic substrate in water. Poly(SUA-H) with sulfonation of 9 mol% bound to the substrate more effectively than that with sulfonation of 29 mol%. These results suggest that hydrophobic interactions between the substrate and the catalyst play important roles for acceleration of the reaction. The substrate molecules are pulled into a proton atmosphere around the poly(SUA-H) molecules by hydrophobic interactions and hydrolyzed in the presence of a high concentration of protons. The observed Michaelis-Menten type catalytic behavior was, however, just the inverse to the ordinary one with respect to the concentrations of the substrate and catalyst. The reaction rate showed a saturation phenomenon with increasing concentration of the catalyst, although the apparent concentrations of the substrate and catalyst were comparable to each other. The kinetically lower concentration of the substrate than the apparent one is inferred to result from the uneven distribution

of sulfonic acid groups in the polymers. The hydrophobic domain having smaller amount of sulfonic acid group interacts stronger with substrate molecules but cannot effectively hydrolyze them, which reduces the effective concentration of the substrate. The amount of such a less effective domain increases with concentration of the catalyst polymer, resulting in decrease in overall catalytic activity.

If the uneven distribution of sulfonic acid groups in the catalyst polymer is improved at an appropriate content of this group, the catalytic activity of the polymer should increase more. Preparation of poly(SUA-H) with even distribution of sulfonic acid group is now under investigation.

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