Ultrasonic Relaxation Study in Aqueous Solutions of Sodium (Carboxymethyl)dextran

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ABSTRACT: Ultrasonic absorption measurements on aqueous solutions of sodium (carboxymethyl)dextran (CMD-Na) were carried out as a function of degree of substitution by sodium carboxymethyl groups over the frequency range 0.5–130 MHz at 25 °C. Effects of the neutralization of (carboxymethyl)dextran (CMD-H) and of the presence of sodium chloride were also studied. The ultrasonic relaxation spectra show two relaxation processes. The relaxation frequencies are located at ~1 and ~20 MHz for all solutions investigated. The relaxation frequency at ~20 MHz shifts to higher and lower frequencies as the polymer chain expands and shrinks, respectively, through the electrorepulsive force of the polyions. This indicates that some local segmental motion of the polymer chain contributes predominantly to the relaxation process among various possible sources. The relaxation process at ~1 MHz is also ascribed to the local segmental motion, although its relaxation amplitude is sensitive to the effect of the protolytic reaction or of the hydrogen bond formation between CH_2COOH groups in CMD-H.

Chemical relaxation studies, including the use of ultrasonic relaxation techniques, have recently proved to be a useful tool to investigate the dynamic properties of polyelectrolyte solutions which are no less important than the static properties in order to understand the solution properties of polyelectrolytes. While some of the dynamic aspects of the properties of polyelectrolyte solutions—for example, the site binding effect and protolytic reactions—have been partly elucidated by a small number of ultrasonic relaxation studies,[1–5] such studies have been limited and a great number of systems have been left uninvestigated. In addition, there has been little work in which a sufficiently wide frequency range has been employed in order to investigate the relaxation spectra. Therefore, studies on various systems covering a wider range of frequencies are needed to obtain a more complete understanding of the dynamic nature of polyelectrolyte solutions. Precise measurements are also required for the same reason.

In our previous paper[5] we have focused our attention on the site binding and protolytic reactions which are coupled with the segmental motion of the polyelectrolyte, and we have studied the ultrasonic relaxation in aqueous solutions of poly(acrylic acid) using precise measurements between 0.8 and 130 MHz.

The charge density of the polyion is also one of the key factors that characterize the solution properties of polyelectrolytes. In the case of solutions of poly(acrylic acid), the charge density of the polyion can be changed by titration of the COOH group, but this methodology is not satisfactory because it makes it more difficult to interpret data when the charge density is modified simultaneously by the presence of the protolytic reaction of the COOH group. Therefore it remains to study the effect of the charge density more directly.

Sodium (carboxymethyl)dextran is a suitable sample for this purpose because one can change only the charge density of polyions by the preparation of samples having various substituted sodium carboxymethyl groups and of

course also by changing the degree of neutralization of the carboxymethyl dextran. In addition, one can take dextran as a reference sample, having no charged groups.

In this article we study the ultrasonic relaxation in aqueous solutions of sodium (carboxymethyl)dextran. The purpose is to present precise ultrasonic absorption measurements over a wide frequency range and to discuss the various contributions (especially the charge density effect) to the ultrasonic relaxation processes.

Materials and Measurements

Materials. (Carboxymethyl)dextran (CMD-H) was prepared by etherification[6,7] of dextran (MW 4.0×10^4) purchased from Pharmacia Fine Chemicals. For the preparation, 32.4 g of dextran was dissolved in 140 cm³ of water with 16 g of NaOH and reacted with 19 g of monochloroacetic acid for 1.5 h at 50–60 °C under continuous stirring. After the reaction, the solution was poured into methanol to precipitate sodium (carboxymethyl)dextran (CMD-Na). The filtered precipitant was dissolved again and was dialyzed and lyophylized. The etherification procedure was repeated several times to obtain CMD-Na, having a higher degree of substitution. CMD-H was finally obtained from CMD-Na by using ion exchange. The titration procedure was used to determine the degree of substitution (D.S.) by carboxymethyl groups and the degree of neutralization (D.N.) of aqueous solutions of CMD-H. Solutions were prepared with freshly distilled water, and all measurements were completed before any aging effect appeared.

Ultrasonic Absorption Measurement. The ultrasonic absorption coefficient, α (Np cm⁻¹), was measured by using a previously described[8] apparatus based on the pulse method over the frequency range 10–210 MHz. In the low-frequency range, 0.5–8 MHz, α was measured by using a cylindrical resonator method under constant temperature maintained to less than $\pm 10^{-3}$ °C. Three types of resonators were used depending on the measured frequency ranges. A more detailed description of the resonators and experimental procedures has been published elsewhere.[9,10] Distilled and degassed water was used as a reference liquid in the resonator method.

Sound Velocity, Density, pH, and Viscosity Measurements. The ultrasonic velocity was mainly measured with cylindrical resonators and occasionally with an interferometer working at a fixed 5.00-MHz frequency. The density was measured with an Ostwald-type pycnometer of 20-mL capacity. The pH values of the solutions were measured with a Model 701 digital pH meter manufactured by Orion Research Inc. An Ubbelohde dilution-type viscometer was used for viscosity measurements. The viscometer was immersed in a bath maintained at a constant temperature of 25.0 ± 0.01 °C.

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Table I
Relaxation Parameters for Aqueous Solutions of CMD-Na with Different Degrees of Substitution at 25 °C (Concentration, 0.095 mol of monomer/L)

D.S.[a]	$10^{17} A_1$, Np·s^2·cm^{-1}	f_{r1}, MHz	$10^{17} A_2$, Np·s^2·cm^{-1}	f_{r2}, MHz	$10^{17} B$, Np·s^2·cm^{-1}	u, m·s^{-1}	$10^5 \mu_{max1}$	$10^4 \mu_{max2}$
0[b]	21.6	1.3	9.6	16.5	23.2	1500	2.06	1.19
0.7	39.7	1.1$_5$	17.3	24	25.1	1503	3.43	3.07
1.2$_5$	57.8	1.0	19.5	28.5	27.5	1505	4.35	4.18
1.6	61.9	0.9	25.5	29	28.0	1506	4.43	5.57
1.8	62.4	0.9	26.7	30	28.4	1507	4.14	6.01
2.0	61.5	0.7	31.8	28	29.3	1508	3.39	6.81
2.2	42.0	0.8	36.0	28	32.0	1509	2.54	7.61

[a] D.S.: degree of substitution. [b] Dextran (MW 4.0 × 10^4).

Data Analysis

The ultrasonic absorption data were analyzed according to eq 1, which assumes either one or two discrete ultrasonic

$$\frac{\alpha}{f^2} = \sum_{i=1}^{2} \frac{A_i}{1 + \left(\dfrac{f}{f_{ri}}\right)^2} + B \qquad (1)$$

relaxation processes where f represents the measured frequency, f_{ri} the relaxation frequency, A_i the relaxation amplitude, and B the contribution to sound absorption from any other process that may be occurring at higher frequencies beyond our frequency range. Equation 1 was fitted by computer to experimental data in the frequency range investigated, and best values of the parameters A_i, f_{ri}, and B were obtained. Further information about the fitting procedure has been presented elsewhere.[5] An equation for double relaxation processes ($i = 1, 2$) was required to successfully fit the sound absorption data in all solutions investigated. Hereafter, suffixes 1 and 2 refer to the low- and high-frequency relaxation processes, respectively.

Since CMD-Na is a polyelectrolyte, it is logical to consider that the ultrasonic relaxation spectra should be expressed by an equation containing a distribution of relaxation times, for example, a Cole–Cole-type equation which is used in the analysis of the dielectric relaxation spectra. Although it has already been found[5] that the Cole–Cole-type equation fails to express the ultrasonic absorption data in aqueous solutions of poly(acrylic acid), the curve fitting was carried out again by using two Cole–Cole-type equations described elsewhere.[5] However, they failed to express successfully the ultrasonic absorption data obtained at frequencies from 7 to 50 MHz.

Results

Figure 1 shows the results of the absoprption measurements for aqueous solutions of CMD-Na having various degrees of substitution by sodium carboxymethyl groups. The ultrasonic absorption coefficient increases with increasing degree of substitution. The data are expressed as α/f^2 vs. logarithmic frequency, $\log f$. For all solutions investigated, α/f^2 decreases with increasing frequency, and this indicates the ultrasonic relaxation phenomena. The solid lines in the figure represent the calculated ultrasonic relaxation spectra from eq 1 and arrows show the location of the relaxation frequencies. Two relaxation frequencies are located at about 1 and 16–28 MHz. The relaxation parameters determined from eq 1 are summarized in Table I where μ_{maxi} is the absorption maximum per wavelength defined as $\mu_{maxi} = A_i f_{ri} u/2$ ($i = 1$ or 2 and u represents the sound velocity). Figure 2 shows the plots of the relaxation frequencies and relaxation strengths, r_i, as a function of degree of substituted sodium carboxymethyl group, where r_i is defined as $r_i = 2\mu_{maxi}/\pi$. There is no great difference
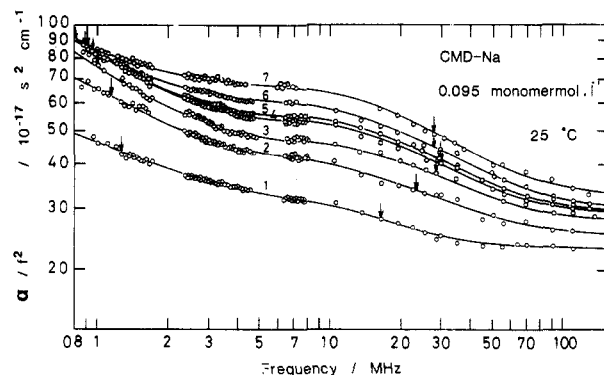

Figure 1. Ultrasonic absorption as a function of frequency for aqueous solutions of CMD-Na having various degrees of substitution at concentration, 0.095 mol of monomer/L: degree of substitution: (1) 0, (2) 0.7, (3) 1.2$_5$, (4) 1.6, (5) 1.8, (6) 2.0, (7) 2.2. The solid lines represent the calculated relaxation spectra from eq 1 and arrows show the location of relaxation frequencies.
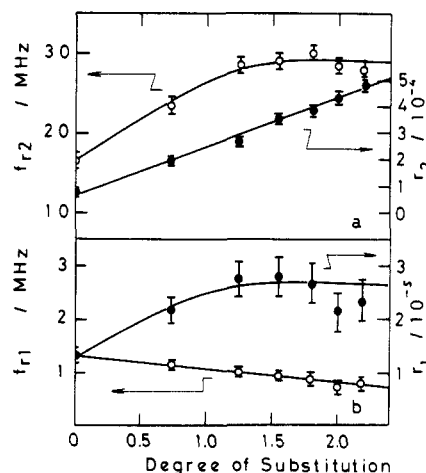

Figure 2. Ultrasonic relaxation frequencies f_{ri} ($i = 1,2$) (O) and relaxation strengths r_i (●) as a function of degree of substitution of CMD-Na.

between the relaxation parameters for a dextran solution and those for CMD-Na solutions in spite of the difference of the nonpolyelectrolyte solution from the polyelectrolyte solutions. For example, the relaxation frequency f_{r2} starts from 16.5 MHz (dextran solution) and smoothly increases with an increase of the degree of substitution and then reaches a constant value above D.S. ca. 1.3. The relaxation strength r_2 also smoothly increases in proportion to the degree of substitution.

Figure 3 shows the ultrasonic relaxation spectra for the aqueous solutions of CMD-Na (D.S. = 2.2) as a function of the degree of neutralization. Reliable ultrasonic absorption measurements were impossible at pHs below 2.4, because of inhomogeneous dissolution of CMD-H. Table

Table II
Relaxation Parameters for Aqueous Solutions of CMD-H (D.S. = 2.2) with Different Degrees of Neutralization at 25 °C
(Concentration, 0.095 mol of monomer/L)

D.N.[a]	pH	$10^{17}A_1$, Np·s²·cm⁻¹	f_{r1}, MHz	$10^{17}A_2$, Np·s²·cm⁻¹	f_{r2}, MHz	$10^{17}B$, Np·s²·cm⁻¹	u, m·s⁻¹	$10^5\mu_{max1}$	$10^4\mu_{max2}$
0	2.45	500	0.9	83.1	12	28.5	1500	33.8	7.47
1.0	4.51	153	0.9	54.0	18.₅	29.0	1503	10.3	7.51
1.6	5.12	82.0	0.9	47.0	21.₅	32.0	1506	5.55	7.61
2.2[b]	8.95	42.0	0.8	36.0	28	32.0	1509	2.54	7.61

[a] D.N.: degree of neutralization. [b] CMD-Na.

Table III
Relaxation Parameters for Aqueous Solutions of CMD-Na (D.S. = 1.6) in the Presence of NaCl at 25 °C

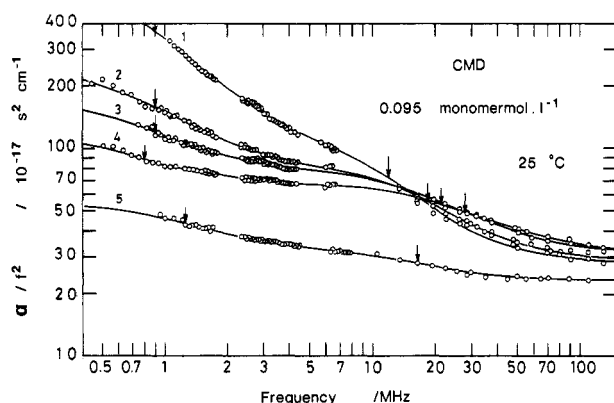| C_{NaCl}/C_{CMD-Na}[a]	$10^{17}A_1$, Np·s²·cm⁻¹	f_{r1}, MHz	$10^{17}A_2$, Np·s²·cm⁻¹	f_{r2}, MHz	$10^{17}B$, Np·s²·cm⁻¹	u, m·s⁻¹	$10^5\mu_{max1}$	$10^4\mu_{max2}$
0	61.9	0.9	25.5	29	28.0	1506	4.43	5.57
5	106	0.9	20.5	20	27.6	1535	7.76	3.19
10	235	0.6	29.0	17.₅	26.0	1563	11.4	3.97

[a] C_{CMD-Na} = 0.095 mol of monomer/L.

Figure 3. Ultrasonic absorption as a function of frequency for aqueous solutions of CMD-H (D.S. = 2.2) having various degrees of neutralization: (1) 0, (2) 1.0, (3) 1.6, (4) 2.2, and (5) dextran.

II lists the relaxation parameters and pH values for the solutions investigated. Figure 4 shows the variations of relaxation frequencies and strengths with the degree of neutralization. The relaxation frequency f_{r2} shifts to high frequency with increasing degree of neutralization, whereas the strength r_2 is independent.

The relaxation spectra for aqueous solutions of CMD-Na (D.S. = 1.6) in the presence of sodium chloride also showed two relaxation processes, and their relaxation parameters are listed in Table III. For the systems with salt, the relaxation frequency f_{r2} decreases with increasing the salt concentration.

Table IV indicates the intrinsic viscosity, [η], of the CMD-Na as a function of the degree of substitution. For the systems without salt, Fuoss' equation[11] was fitted to the viscosity data in order to determine the intrinsic viscosity as [η] = A + D, where A and D are the parameters in the Fuoss equation:

$$\eta_{sp}/c = \frac{A}{1 + Bc^{1/2}} + D \tag{2}$$

η_{sp}, c, and B represent the specific viscosity, concentration, and a parameter, respectively. For the systems with salt, [η] was determined by the usual relation

$$[\eta] = \lim_{c \to 0} \eta_{sp}/c \tag{3}$$

The intrinsic viscosity gradually increases with increasing degree of substitution for the systems without salt and then reaches a constant value above D.S. = 1.8. An increase of
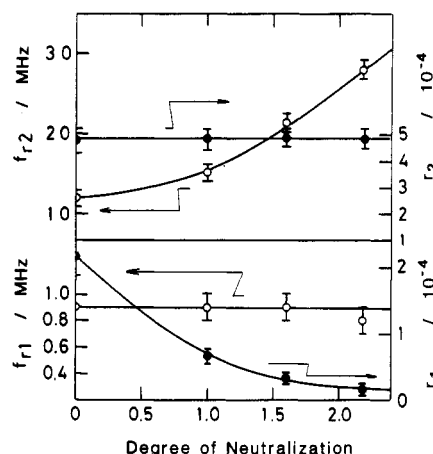

Figure 4. Ultrasonic relaxation frequencies f_{ri} (O) and relaxation strengths r_i (●) as a function of degree of neutralization of CMD-H (D.S. = 2.2).

Table IV
Intrinsic Viscosity for CMD-Na as a Function of Degrees of Substituted Carboxymethyl Group in Aqueous and NaCl Aqueous Solutions at 25 °C

D.S.	[η]	D.S.	[η]
0[a]	0.21	1.8	99
0.25	18	2.0	100
1.5	83, 0.50,[b] 0.23[c]	2.2	102

[a] Dextran. [b] 0.1 M NaCl solution. [c] 1.0 M NaCl solution.

[η] with the degree of substitution indicates that the CMD-Na chain expands gradually as the charge density of the polyion increases. It is noted that the value of [η] for dextran (0.21) is nearly equal to that for CMD-Na (D.S. = 1.5) in 1.0 M NaCl aqueous solution.

Discussion

The following are the general trends of various ultrasonic relaxation spectra of polymer solutions which have been investigated by us.[5,8,9,12-14] (1) All relaxation spectra can be expressed sufficiently by using a discrete two-step Debye-type equation with only one exception, cellulose acetate in cyclohexanone.[9] (2) Locations of relaxation frequencies do not differ very much in the polymer solutions investigated in spite of the various structural differences and differences of flexibility of the polymer chains. They are at ~1 and 10–20 MHz, respectively, without distinction of polyelectrolyte or nonpolyelectrolyte solu-

tions. (3) The relaxation frequencies are independent of the molecular weight. (4) The relaxation strengths depend on the concentration of polymer solute and the properties of solvent.

In order to explain these general observations, we have considered that local segmental motions may contribute predominantly to the ultrasonic relaxation processes in polymer solutions. A comparison of the relaxation parameters for the CMD-Na solutions with these trends leads us to conclude that the observed relaxation processes can be ascribed as well to the local segmental motion. This assignment is also supported by the following independent information. (1) The relaxation spectra for the solutions of CMD-Na do not differ much from the spectrum for the solution of dextran in their shapes and the locations of relaxation frequencies (Figures 2 and 4). This implies that possible sources of the relaxation phenomena peculiar to the polyelectrolyte solutions make only a slight contribution to the relaxation processes observed here. The motion of the side chain, CH_2COONa, is ruled out because the two relaxation processes are already observed in the aqueous solution of dextran which has no side chain. The side chain does not contribute very much to the relaxation frequencies but the relaxation strengths, especially r_2, increase proportionally by ca. 2.9×10^{-4} per degree of substitution. (2) The relaxation frequency f_{r2} shifts to higher frequencies as the degree of substitution, and thus the charge density of the polymer chain, increases. One might imagine that the local segmental motion of CMD-Na becomes easier as the polymer chain is gradually expanded by an electrorepulsive force with increasing charge density. The viscosity measurements directly indicate the gradual expansion of the polymer chain (Table IV). (3) The results of the neutralization and added salt studies are readily explained on the basis of the generally accepted observation that the polyelectrolyte chain shrinks with addition of salts[15,16] and expands with increasing degree of neutralization.[17-19] The frequency shifts of f_{r2} in the neutralization and the added salt studies are consistent with this fact because the f_{r2} shifts to low and high frequency as the salt concentration and degree of neutralization increase, respectively (Tables II and III). (4) For two systems having similar intrinsic viscosities, their relaxation frequencies f_{r2} are also located at the similar frequencies. CMD-Na in 1.0 M NaCl solution has a similar magnitude of intrinsic viscosity to that of dextran in aqueous solution (Table IV). Moreover, f_{r2} for a CMD-Na solution with salt $C_{NaCl}/C_{CMD-Na} = 10$ (this ratio of the concentrations is nearly equal to that of the solution of CMD-Na in 1.0 M NaCl) is approximately equal to that for the aqueous solution of dextran (Tables I and III).

We have found in our previous work[20] that aqueous solutions of cyclodextrins (cycloamyloses) show two ultrasonic relaxation processes in the frequency range 0.8–135 MHz. Therefore, we estimate that a segment consisting of at least six or more glucose units may be involved in the relaxation processes observed here. Because of the various and complex nature of the segmental motions in polymer solutions, we hesitate to proceed with further assignments until a clearer picture of the segmental motion is forthcoming, conceivably from independent studies. It is clear that additional information is required to make an unequivocal identification for the observed relaxation processes with the possible segmental motion.

The relaxation process due to the protolytic reaction appears in aqueous solutions of poly(acrylic acid)[5] and in solutions of polypeptide or protein[21,22] at frequencies below 10 MHz. In these solutions, this process overlaps the relaxation processes associated with the segmental motion

of polymer chain. Moreover, aqueous solutions of univalent and divalent carboxylic acids also show relaxation processes in the megahertz region arising from protolytic reactions[23,24] or hydrogen bond formation.[4,25] The results of these previous studies lead us to consider that protolytic reactions or hydrogen bond formation between carboxymethyl groups should make some contribution to the relaxation amplitude of the low-frequency relaxation process observed in aqueous solutions of CMD-H. Also, the aqueous solution of CMD-H shows a sharp increase of the ultrasonic absorption at frequencies below 10 MHz. The difference between the relaxation spectrum of a solution of CMD-H (D.N. = 1.6) and that of a solution of CMD-Na (D.S. = 1.6) (Figures 1 and 3) can also be attributed to the existence of the contribution mentioned above because the relaxation spectra should coincide with each other if they are defined only by the contributions of the charge density and the segmental motion. The lack of definite information about intramolecular protolytic reactions and hydrogen bond formation in the polyelectrolyte solutions, however, makes it at present impossible to analyze quantitatively for these contributions.

Zana and Tondre have found[1] two ultrasonic relaxation processes due to site binding of counterions to polyion in a series of polyphosphate solutions. The site binding of Na^+ on the polyion will be discussed here since it is one of the possible sources of the ultrasonic relaxation processes observed in this study.

As already pointed out above, the relaxation spectra of solutions of CMD-Na do not differ much from the spectra of aqueous solution of dextran in their shapes and the locations of the relaxation frequencies. This means that the contribution of the site binding to the relaxation processes observed here is very small. Moreover, a simple analysis for concentration dependence of relaxation frequency indicates that the relaxation frequency should shift to the high-frequency side with an increase of Na^+ concentration if site binding contributes predominantly to the ultrasonic relaxation process. On the other hand, f_{r1} is independent of the degree of neutralization (Figure 4) and tends to decrease slightly with increasing degree of substitution (Figure 2). The relaxation frequency f_{r2} also should shift to high frequency when both degrees of substitution and neutralization increase, but be independent of the degree of neutralization (Figure 4). These frequency shifts of f_{r1} and f_{r2} also mean that the contribution of the site binding of Na^+ is very small. In aqueous solutions of poly(acrylic acid) also,[5] the site binding between polyion and Na^+ makes only a slight contribution to the ultrasonic relaxation process in the megahertz region. Although it is still unclear why the contribution is so small in these solutions, the volume change associated with site binding of Na^+ may be too small to give rise to the ultrasonic relaxation process.

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Pulse Radiolysis Study on Organopolysilane Radical Anions

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ABSTRACT: Poly(methylpropylsilane) (PMPrS) and poly(methylphenylsilane) (PMPS) were investigated by pulse radiolysis with 2-ns time resolution. PMPrS and PMPS solutions in tetrahydrofuran (THF) exhibit strong single absorption bands at 363 and 372 nm, respectively, in the transient spectra. These transient species react with pyrene to produce pyrene radical anions. They also decay in reaction with added CHCl₃. Chloromethylated PMPS does not exhibit such a transient absorption, indicating that electron dissociative attachment occurs. These facts indicate that the observed transient species are radical anions. The polymer radical anions have a long lifetime and do not decay within 150 ns. The extinction coefficients of PMPrS and PMPS radical anions are both $(1.6 \pm 0.2) \times 10^5$ M^{-1} cm^{-1}. The electron-transfer rate from polymer radical anions to pyrene is $(1.2 \pm 0.1) \times 10^{10}$ M^{-1} s^{-1} for PMPrS and $(1.4 \pm 0.2) \times 10^{10}$ M^{-1} s^{-1} for PMPS. The reaction rate of PMPrS with the solvated electron in THF is $(3.4 \pm 0.5) \times 10^9$ M^{-1} s^{-1}.

Introduction

Organopolysilanes have unique optical properties. They have strong UV absorption bands in the 300–360-nm region,[1] which has been attributed to σ–σ* or σ–3π transitions.[2-4] As the chain length increases, they show a bathochromic shift which is thought to arise from delocalization of the σ electrons.[5] Although organopolysilanes consist of Si–Si single bonds, they resemble carbon conjugative compounds. Extended Hückel MO calculation has shown that cyclic organopolysilanes have similar energy levels to benzene.[6] Recently, poly(methylphenylsilane) has been found to exhibit nonlinear optical properties.[7]

Si–Si bonds of organosilanes are broken by UV irradiation to produce radical fragments or silylene.[8] This photoreaction and the photoinduced radical species have been thoroughly investigated in terms of their application to photoresists.[9-11] Concerning their ionic states, cyclic organopolysilanes, such as $(Si(CH_3)_2)_n$ ($n = 4$–6) and $(Si(C_6H_5)_2)_m$ ($m = 4, 5$), form radical anions by reduction with alkali metal[6,12-14] and radical cations by oxidation with AlCl₃.[15] ESCA studies have shown that unpaired electrons of these ions are delocalized over the ring skeleton. Properties of ionic states of linear organopolysilanes have not yet been reported. If they are ionized, the unpaired electron is expected to be delocalized along the polymer chain. The electric properties of linear organopolysilanes seem interesting from the viewpoint of their potential semiconductivity.[16]

This report deals with radical anions of high molecular weight linear organopolysilanes, poly(methylpropylsilane) (PMPrS) and poly(methylphenylsilane) (PMPS). Their optical properties and kinetics were determined by means of pulse radiolysis.

Experimental Section

PMPrS and PMPS were prepared according to the method previously reported.[17] Molecular weight was measured by gel permeation chromatography (GPC) on the basis of the standard polystyrene. Weight average molecular weight (M_w) and polydispersity (M_w/M_n) of PMPrS were 2.1×10^4 and 2.1 and those of PMPS were 22.4×10^4 and 5.7. Chloromethylated PMPS (CMPMPS) was also prepared according to the method used for the chloromethylation of polystyrene[18] and poly(diphenylsiloxane).[19] Two grams of PMPS was dissolved in a mixture of 20 mL of chloromethyl methyl ether and 20 mL of chloroform. Two grams of SnCl₄ was slowly dropped into the solution at 0 °C. After stirring for 15 h at 5 °C, the solution was poured into methanol to obtain CMPMPS. CMPMPS was refined by sedimentation twice with tetrahydrofuran (THF)–methanol. The yield was 90%. M_w and M_w/M_n of CMPMPS were 2.7×10^4 and 2.4, respectively. Chloromethyl groups are thought to attach on para or ortho positions of phenyl groups by the Friedel–Crafts reaction.