2956 *Macromolecules* **1997,** *30,* 2956−2962

Characteristic Vibrational Spectral Change Observed for the π-Conjugated Structure of Sulfonated Polyethylene

Kohji Tashiro,*,† Takeru Kitashoji,‡ and Jyoji Ihata§

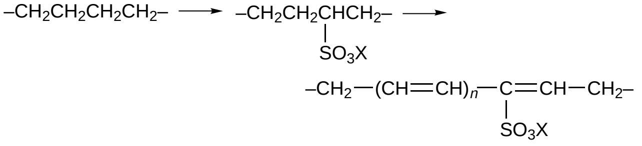
Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560, Japan; NARD Laboratory, Co. Ltd., Amagasaki, Hyogo 660, Japan; and SP-21 Center Corporate R&D Administration, Asahi Chemical Industry Co., LTD., Fuji, Shizuoka 416, Japan

Received January 22, 1997; Revised Manuscript Received March 18, 1997⊗

ABSTRACT: Infrared-active SO stretching bands [ν(SO)] observed for the sulfonated polyethylene (PE) samples were found to change their vibrational frequencies systematically depending on the degree of the π-conjugated chain structure generated through the sulfonation reaction and also on the sulfonate ion species SO_3X in the structure [−CH═CH−CH═CH−CH═C(SO_3X)−C═C−...], where X = H, Na, Li, K, Ca, and Zn. For the sulfonated PE samples with SO_3Na groups, the ν(SO) band was found to shift to the higher frequency side as the conjugated chain length was increased. When the π-conjugated chain structure was modified by bromination reaction (...−C═C−C═C−C═C−C═C−... + Br_2 → ...−C═C−C═C−CBr−CBr−...), such a high-frequency shift was canceled. The sulfonated PE samples with SO_3H groups, on the other hand, did not show any high-frequency shift even for longer π-conjugated chain structure but gave the ν(SO) bands at the position rather close to those of the SO_3Na species coupled with a short π-conjugated chain. These spectral changes were confirmed also by measuring the spectral changes for a series of the model compounds having the π-conjugated structure combined with the SO_3Na groups.

Introduction

It has been reported by Ihata[1−3] that, when polyethylene (PE) films are sulfonated by an application of SO_3 gas species, the skeletal chains change into the electronically conjugated structure ...C═C−C═C−C═... as shown below.



$$-CH_2CH_2CH_2CH_2- \longrightarrow -CH_2CH_2\underset{\displaystyle SO_3X}{\underset{|}{C}}HCH_2- \longrightarrow -CH_2-(CH{=}CH)_n-\underset{\displaystyle SO_3X}{\underset{|}{C}}{=}CH-CH_2-$$

This finding was made through the several experiments including the visible−ultraviolet (VUV) and resonance Raman spectral measurements. For example, the C═C stretching Raman band around 1600 cm^{-1} was found to shift to the lower frequency side as the sulfonation reaction proceeded, indicating a growth of the π-conjugated segments within the PE skeletal chains. The infrared spectra were also found to change with the sulfonation reaction. Ihata noticed an apparently curious phenomenon such that the infrared bands intrinsic to the sulfonate groups shift to the “higher” frequency side with an increment of the π-conjugated length in the PE chains. The vibrational frequency of the sulfonate bands may shift to the “lower” side because the S−O bond strength should be weaker if the resonance structure C═C−S═O ↔ C−C═S−O is accepted. The actual observation is against this prediction: the S−O stretching bands are observed at a higher frequency position for the structure $(-C{=}C-)_n-SO_3Na$. In addition, as will be described in this paper, it was also found that the peak is observed at the lower frequency side for the structure $(-C{=}C-)_n-SO_3H$. Why is such a different behavior observed between the SO_3Na and SO_3H species? In order to clarify this curious phenomenon itself in the sulfonated PE films, we need to reconfirm the phenomenon more definitely. In this paper we will report the details of the infrared spectral change observed during the sulfonation reaction of PE. At the same time we will examine the various factors governing the vibrational frequency shift of the SO_3 bands from various points of view.

Experimental Section

Samples. The samples used here were commercially available high-density PE films with a thickness of ca. 10 μm.

Sulfonation. Sulfonation of the PE films can be made by the various types of methods:[1−6] for example, an exposure of films into an organic solution of SO_3 for a predetermined time or a direct exposure of films into SO_3 gas atmosphere. In the present study the former method was employed because of its mild and homogeneous sulfonation condition. γ-type SO_3 liquid was dissolved into dichloroethane (DCE) at a concentration of 20 or 40 wt % at room temperature, where the γ form was used because of its high efficiency for the sulfonation reaction among the various types of SO_3 species such as α (solid), β (solid), and γ (six-membered ring, liquid) forms. Several PE films of 5 × 5 cm^2 area were immersed into the DCE−SO_3 solution with one end of the films tensioned vertically by applying a weight. After a predetermined time of immersion, each film was taken out successively and washed in DEC solvent and then in water. Depending on the treatment condition, the sulfonate groups of the PE films change their ionic form: i.e., the PE samples with SO_3H species were obtained by washing in water, while the films with SO_3Na species were obtained when washed in NaOH aqueous solution of ca. 1 N concentration. The films were then dried and supplied to the infrared measurement.

Bromination of Sulfonated PE Films. In order to check the effect of π-conjugated structure on the frequency shift of the SO_3X groups, the double bonds were reduced to C−C bonds by bromination reaction. The bromination was made by immersing the sulfonated PE films into 5 vol % Br_2−CCl_4 solution for 28 h at room temperature.[7]

FTIR Measurements. The Fourier-transform infrared (FTIR) spectra were measured for the thus obtained films by

---

* To whom correspondence should be addressed.

† Osaka University.

‡ NARD Laboratory, Co. Ltd.

§ Asahi Chemical Instry Co., LTD.

⊗ Abstract published in *Advance ACS Abstracts,* May 1, 1997.

S0024-9297(97)00062-4 CCC: $14.00

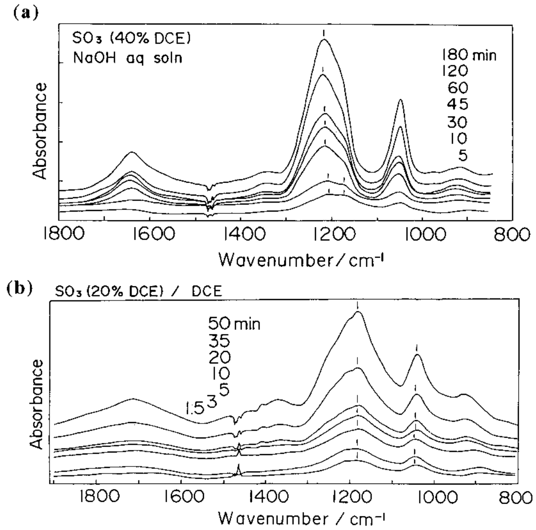


Figure 1. (a) FTIR spectra of polyethylene films sulfonated for different reaction times by SO_3–dichloroethane (DCE) solution followed by washing in NaOH aqueous solution (PE–SO_3Na). The spectrum of the unreacted PE film was subtracted from the original spectra. (b) Same for PE–SO_3H species, which were obtained by sulfonation and washing with DCE.

using a Japan Spectroscopic Company FT-IR 8300 spectrometer with resolution power 2 cm^{-1}. The ATR (attenuated total reflection) spectra were also measured, where the KRS5 single crystal was used as an internal element.

Results and Discussion

Vibrational Spectra of Sulfonated PE Films. (1) FTIR. In Figure 1 is shown the time dependence of the FTIR spectra measured for the sulfonated PE films after being dipped into the reaction reservoir for a predetermined time. Figure 1a shows the case of the PE films with SO_3Na groups [PE–SO_3Na], which were obtained by immersing the sulfonated samples into NaOH aqueous solution. In order to make the change of the sulfonate bands clearer, the IR bands originating from the unreacted PE were subtracted from the original spectra. As the sulfonation reaction proceeds, the band around 1630 cm^{-1} was found to increase the intensity largely, which is assignable to the OH deformation mode [δ(OH)] of the water molecule absorbed in the sulfonated PE. In the frequency region 900–1300 cm^{-1} the large increase of the intensity is observed for the sulfonate bands of symmetric (1050 cm^{-1}, $\nu_s(SO_3)$) and antisymmetric (1200 cm^{-1}, $\nu_{as}(SO_3)$) stretching modes. In Figure 2 is plotted the reaction-time dependence of the integrated intensity evaluated for the various bands shown in Figure 1. The band intensity of the sulfate group increases rapidly in the early 30 min and slows down gradually after 1 h. In Figure 3a the enlarged spectra are shown for PE–SO_3Na samples so as to make the peak positional change more clearly. The weak bands are observed at 1170 cm^{-1} [$\nu_{as}(SO_3)$] and 1040 cm^{-1} [$\nu_s(SO_3)$] in an early stage of the reaction. But, after the reaction proceeds further, the new and intense bands begin to appear in a higher frequency region (1225 and 1050 cm^{-1}) and so the total band profiles look apparently to shift the peak position to the higher frequency side. In Figures 1b and 3b are shown the FTIR spectra taken for the PE-SO_3H films with SO_3H groups as the side chains, which were obtained by washing the sulfonated films in water and drying in air. The δ(OH) band is broader and observed at a higher frequency position than that of PE–SO_3Na, suggesting weaker OH···OS hydrogen bonding for SO_3H species compared with the case of SO_3Na species. In contrast to the latter case, remarkable spectral change is not observed and the intensity increases with the whole spectral profile almost unchanged. Rather the peak positions seem to shift to the lower frequency side although the degree is not very high. The spectral profile of PE–SO_3H is rather similar to that of PE–SO_3Na obtained at an early stage.

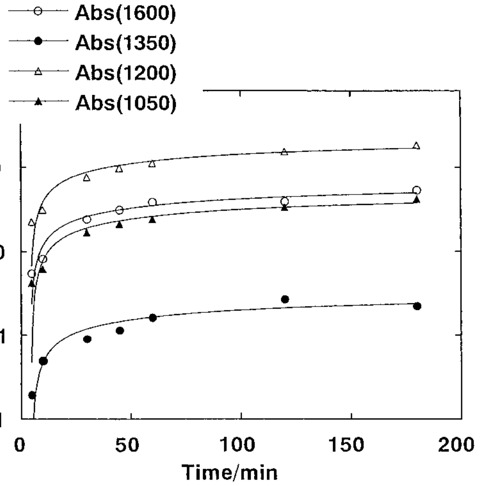


Figure 2. Increase of the intensity of the infrared bands associated with the sulfonate groups as a function of the sulfonation reaction time.

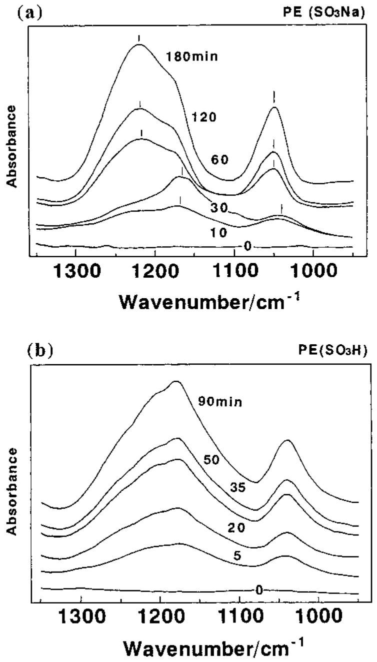


Figure 3. Infrared spectral change in the frequency region 1300–1000 cm^{-1} measured for the PE films sulfonated for the period indicated: (a) PE–SO_3Na and (b) PE–SO_3H species. The spectrum of the original PE film was subtracted from all the spectra.

Figure 4 shows a series of spectra in the frequency region 1400–400 cm^{-1} observed for PE–SO_3Na samples. In parallel to the intensity increment of the sulfonate group bands, the weak bands are observed at 940 and 980 cm^{-1}, which are assigned to the C=C wagging modes ω(C=C). Increase of the ω(C=C) band intensity is accompanied by a remarkable change in the sample color: from a colorless and semitransparent state to pale green, pale brown, brown, dark brown, and brownish black. Ihata measured the resonance Raman spectra of these colored samples[1] and found a lower frequency

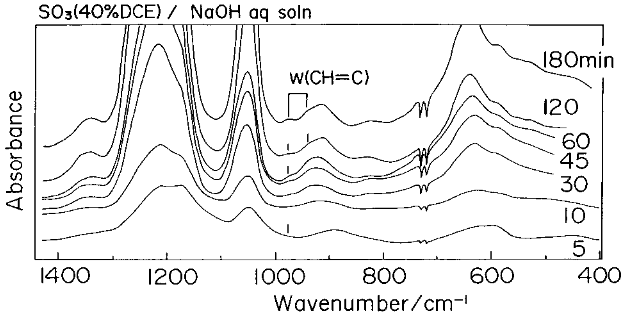


Figure 4. Infrared spectral change in the frequency region 1400−400 cm^{-1} measured for the PE films sulfonated for the period indicated. The samples were PE−SO_3Na type. The intensity change of the wagging band of the CH=CH group is emphasized. The spectrum of original PE film was subtracted from all the spectra.

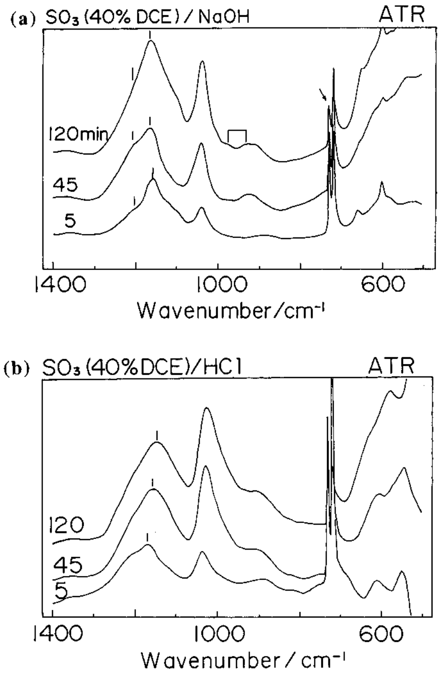


Figure 5. ATR spectral change measured for (a) the PE−SO_3Na samples and (b) the PE−SO_3H samples. The relative intensity of the sulfonate bands is different from that measured by the transmission mode (for example, Figures 1 and 3), possibly because of the difference in chain orientation between the bulk and surface regions.

shift of the C=C stretching band for more deeply sulfonated PE samples. At the same time, the VUV spectra also change their peak positions with progression of the sulfonation reaction. These experimental data indicate a growth of the π-conjugated skeletal chain.

(2) ATR Spectra. The sulfonation reaction is considered to start from the surface and progress to the inner part of the sample as the SO_3 gas diffuses gradually into the sample. In such a case, a more remarkable spectral change may be observed when the film surface is searched by such a technique as attenuated total reflection (ATR) spectroscopy. Figure 5 shows the ATR spectra measured for the sulfonated PE samples. As seen in Figure 5a, the $\nu_{as}(SO_3)$ band is observed at 1170 cm^{-1} for the PE−SO_3Na sulfonated for 5 min, which shifts to a higher position (ca. 1180 cm^{-1}) and increases in intensity for the sample treated for longer reaction time. At the same time the band (shoulder) at 1200 cm^{-1} also increases in intensity. The bands of ω(C=C) are also observed for the sample sulfonated for 120 min. On the other hand, in the ATR spectra of PE−SO_3H shown in Figure 5b, as the sulfonation reaction progresses, the peak position shifts to the "lower" frequency side for both the bands $\nu_{as}(SO_3)$ and $\nu_s(SO_3)$. This low-frequency shift observed for the PE−SO_3H sample is in contrast to the high-frequency shift in the PE−SO_3Na sample.

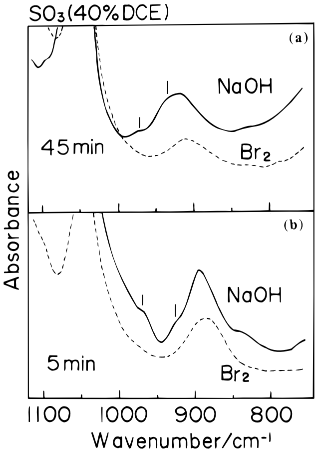


Figure 6. Infrared spectral change measured before and after bromination reaction of sulfonated PE films (PE−SO_3Na type). The sulfonation reaction time is (a) 45 min or (b) 5 min. The vertical bars indicate the disappearance of the ω(C=C) bands after bromination reaction.

Additional Experimental Support for the Intimate Relation between the Skeletal π-Conjugation and the Vibrational Frequency Shift of the SO_3 Bands. (1) Bromination Reaction. On the basis of all these experimental results, we may conclude that the formation of a C=C conjugated structure occurs at the same time as the sulfonation reaction of the PE chains. That is to say, as the sulfonation reaction proceeds further, the amount or length of the C=C conjugated bonds increases further, as clarified by the measurements of IR, VUV, and resonance Raman spectra. Besides, we should notice that the vibrational frequencies of the SO_3 bands change their values depending on the degree of sulfonation or the π-conjugated length as well as the type of SO_3 species, SO_3Na or SO_3H.

In order to confirm the relationship between the degree of π-conjugated length and the frequency positions of the SO_3 IR bands, we tried to reduce the C=C bonds to C−C bonds, which might result in the lower shift of the SO_3 band frequency. The reduction was carried out through the bromination reaction: that is to say, the sulfonated PE sample films were dipped in the carbon tetrachloride solution of Br_2 (5 vol %) for 28 h and dried at 60 °C after being washed in carbon tetrachloride.[7] The bromination reaction caused the change of color of the sample from brownish black to pale brownish, indicating a decrease in the π-conjugation length through the bromination reaction C=C → CBr−CBr. Figure 6 shows the infrared spectral change in the ω(C=C) mode region before and after the bromination reaction of the PE−SO_3Na film. For both the PE films sulfonated for a short time (5 min) and a long time (60 min), the ω(C=C) bands disappear after bromination treatment. In Figure 7 are shown the transmission spectra measured for the PE films before and after bromination: the original films were PE−SO_3-Na which were (a) lightly (5 min) or (b) heavily (45 min) sulfonated. In case a, the spectral profile did not change essentially even after bromination for both samples. On

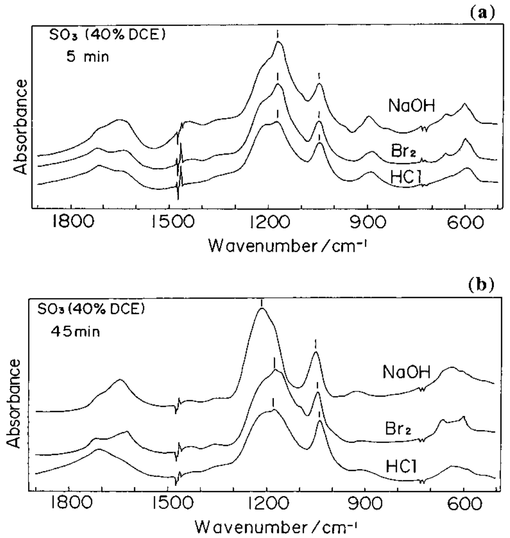


Figure 7. Comparison of the infrared spectra for PE$-SO_3$-Na (indicated as NaOH), PE$-SO_3H$ (indicated as HCl), and the brominated sample of PE$-SO_3Na$ type (indicated as Br_2). The samples were sulfonated for a period of (a) 5 min or (b) 45 min.

the other hand, for the heavily sulfonated samples (b), the SO_3 bands characteristic of the long conjugated structure decrease drastically in intensity and the bands apparently shift to the lower frequency side after the bromination reaction: the spectra became very similar to those of PE$-SO_3H$ and the lightly sulfonated PE$-SO_3Na$. (Strictly speaking some new bands can be detected as a lower-side shoulder of the intense 1200 cm^{-1} band, as seen in Figure 7b. Addition of bromine atoms to the skeletal chain may naturally cause some change of the vibrational modes and vibrational frequencies.) This indicates clearly that the shortening of the π-conjugated system by bromination reaction results in the recovery of the infrared spectra characteristic of the lightly sulfonated PE samples. In this way the intimate relationship between the conjugation length and the frequency shift of the $\nu_{as}(SO_3)$ and $\nu_s(SO_3)$ bands has been confirmed: the longer conjugation structure gives the $\nu_{as}(SO_3)$ and $\nu_s(SO_3)$ bands at higher frequency positions as long as the PE$-SO_3Na$ samples are concerned.

More drastic change can be detected by measuring the ATR spectra, because the structural change occurring on the surface region is detected selectively. In fact, as shown in Figure 8b, the clear change was detected for the ATR spectra taken for the bromine-treated sample films. The band peaks are detected on the low-frequency side compared with those of the original samples. This might come more from the change in the chemical structure on the surface area; for example,

$$\ldots{-}CH{=}CH{-}CH{=}C(SO_3X){-}CH{=}CH{-}\ldots \rightarrow$$
$$\ldots{-}CHBr{-}CHBr{-}CHBr{-}$$
$$-C(SO_3X)Br{-}CHBr{-}CHBr{-}\ldots$$

In Figure 8a no remarkable change is detected even after bromination for the PE-SO_3Na samples prepared in a short time because of the small number of C=C bonds.

(2) Low-Molecular-Weight Model Compounds. In the previous sections the relationship between the C=C conjugated chain length and the vibrational frequencies of sulfonate groups has been clarified. In order to confirm this relationship more tightly, it may be useful to investigate the vibrational spectra of the low-molecular-weight model compounds having the various lengths of the conjugated chain coupled with the SO_3X groups. We synthesized or purchased the following compounds and measured the FTIR spectra for the SO_3-Na and SO_3H species. The procedure of synthesizing these compounds is described in Scheme 1.[8-10]

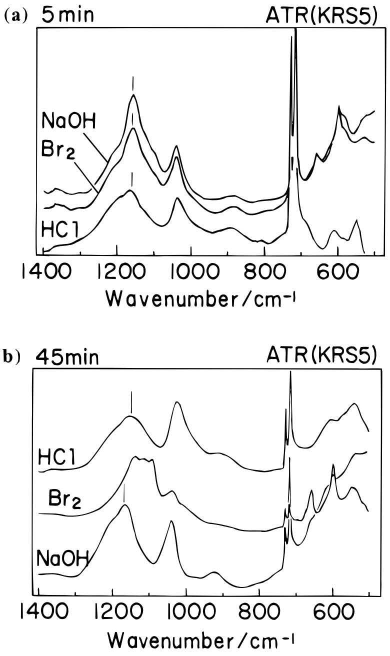


Figure 8. Comparison of the ATR spectra for PE$-SO_3Na$ (indicated as NaOH), PE$-SO_3H$ (indicated as HCl), and the brominated sample (indicated as Br_2) of PE$-SO_3Na$ type. The samples were sulfonated for a period of (a) 5 min or (b) 45 min.

(**a**) $CH_3CH_2CH_2CH_2CH_2{-}SO_3X$ (X = H or Na)

(**b**) $CH_3CH_2CH_2CH{=}CH{-}SO_3X$

(**c**) $CH_2{=}CH{-}CH{=}CH{-}SO_3X$

(**d**) $XO_3S{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}SO_3X$

These compounds correspond, respectively, to the chain segments of zero, one, two, and three C=C conjugated units connected to the sulfonate group. Figures 9−11 show the FTIR spectra of the three compounds **a**−**c** with SO_3Na or SO_3H groups. The spectra of the compound **d** were already reported in ref 3. For all the compounds indicated above, the δ(OH) band in the region 1500−1900 cm^{-1} and the $\nu_{as}(SO_3)$ and $\nu_s(SO_3)$ bands around 1000−1300 cm^{-1} are different largely between the SO_3Na and SO_3H species. In particular, the SO_3Na species shows the $\nu_{as}(SO_3)$ and $\nu_s(SO_3)$ bands in a higher frequency region compared with that for the SO_3H species, except for the case of *n*-pentanesulfonate (**a**). These spectral behaviors indicate that the coupling between the π-conjugated group and the SO_3X group affects the spectral pattern largely.

In Figures 12 and 13 are compared respectively the spectra of SO_3Na and SO_3H species for various compounds with different conjugated lengths. In the case of SO_3Na species shown in Figure 12, the band profile changes depending on the π-conjugated length. For the heavily sulfonated PE$-SO_3Na$ and compound **d**, the profiles are close to each other. For compounds **b** and

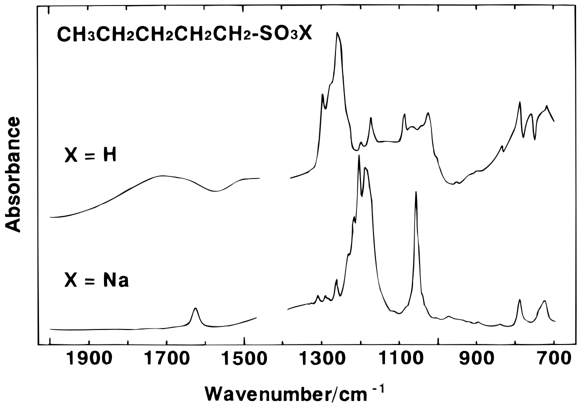


Figure 9. Infrared spectra of *n*-pentanesulfonate with the ionic group Na or H.

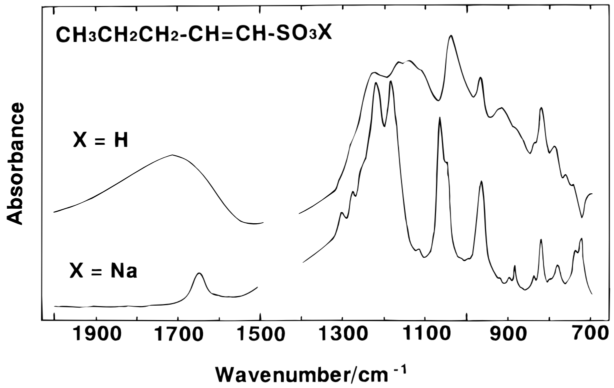


Figure 10. Infrared spectra of 1-pentenesulfonate with the ionic group Na or H.

c, the peak height of the band around 1210 cm^{-1} (as shown by the vertical line) is relatively low compared with those of the above-mentioned two samples. For compound **a**, the 1210 cm^{-1} band disappears and the two intense bands are observed around 1180 cm^{-1}. Although we cannot assign these bands clearly, the higher frequency component (or the left-sided band at 1190 cm^{-1}) might correspond to the low-frequency shift of the $\nu_{as}(SO_3)$ band observed for the other compounds. As a whole the $\nu_s(SO_3)$ band does not change its position very much, but compound **c** with a shorter conjugation length shows the band at a slightly lower frequency position than those of compound **d** and the heavily sulfonated PE sample. Compounds **a** and **b** show the corresponding band at higher positions than those of compounds **c** and **d**. The different symmetry among these compounds might change the infrared activity, and so the number and relative intensity of the possible bands are different from each other, making the spectral profile complicated in a different manner. At present we cannot discuss in detail why the band position is higher for compounds **a** and **b** than for **c** and **d**.

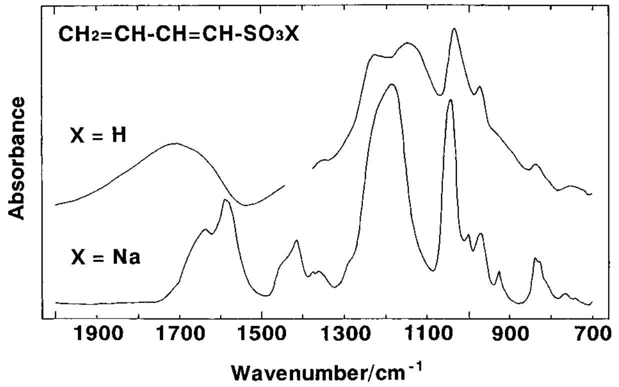


Figure 11. Infrared spectra of 1,3-butadienesulfonate with the ionic group Na or H.

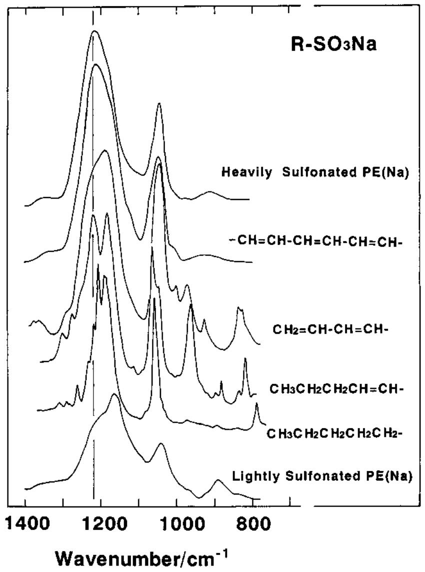


Figure 12. Comparison of the infrared spectra measured for a series of model compounds R−SO3Na with the R group indicated and the PE−SO3Na samples sulfonated heavily or lightly.

In Figure 13 of the SO3H species, the bands of the $\nu_{as}(SO_3)$ and $\nu_s(SO_3)$ modes are observed almost in common for all the compounds with different conjugated lengths. The spectral profile of compound **a** is quite different from those of the other members, but the reason is difficult to obtain.

All these spectral data of the low-molecular-weight model compounds may make us confirm the phenomena

Scheme 1. Brief Description of the Synthesis of Low-Molecular-Weight Model Compounds of Sulfonated PE

(1) 1-Pentenesulfonate

$$CH_3CH_2CH_2CH{=}CH_2 \xrightarrow{\text{benzoyl peroxide}} CH_3CH_2CH_2CH(Cl)CH_2SO_2OCH_3 \xrightarrow{NaI/Me_2CO}$$

$$CH_3CH_2CH_2CH(Cl)CH_2SO_2ONa \xrightarrow{PCl_5} CH_3CH_2CH_2CH(Cl)CH_2SO_2Cl \xrightarrow{Et_3N,\ C_6H_6}$$

$$CH_3CH_2CH_2CH{=}CHSO_2Cl \xrightarrow{NaHCO_3/H_2O} CH_3CH_2CH_2CH{=}CHSO_3Na$$

(2) Butadiene-1-sulfonate

$$CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{\text{(i) } SO_3\text{-pyridine; (ii) } Ba(OH)_2} (CH_2{=}CH{-}CH{=}CH{-}SO_3)_2Ba \xrightarrow{\text{ion-exchange regin}}$$

$$CH_2{=}CH{-}CH{=}CH{-}SO_3H \xrightarrow{NaOH} CH_2{=}CH{-}CH{=}CH{-}SO_3Na$$

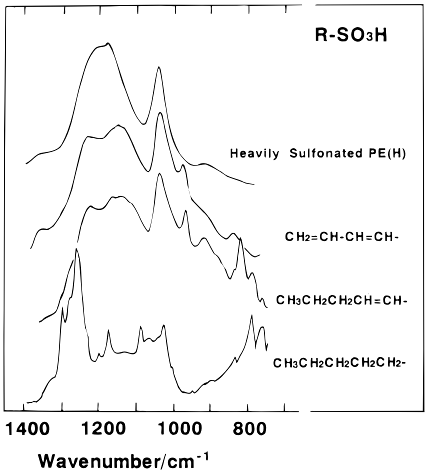


Figure 13. Comparison of the infrared spectra measured for a series of model compounds R$-$SO$_3$H with the R group indicated and the PE$-$SO$_3$Na sample sulfonated heavily.

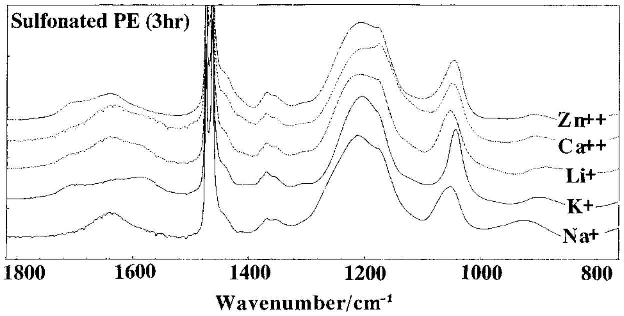


Figure 14. Infrared spectra of PE$-$SO$_3$X samples with X = Na$^+$, K$^+$, Li$^+$, Ca^{2+}, and Zn^{2+}. The original samples were sulfonated for 3 h.

observed for sulfonated PE samples: the sulfonate bands shift their position with a change in the π-conjugated length of the skeletal chain for the SO$_3$Na species, while the SO$_3$H species do not show any large shift in the band position irrespective of the π-conjugation length.

Effect of Metal Ion Species of the Sulfonate Group. As seen in the previous sections, the vibrational spectra of the sulfonated PE samples change their profiles depending on the type of the sulfonate group, SO$_3$Na or SO$_3$H. We may naturally expect that the spectra are changeable by modifying the metal ion species of the sulfonate group to the other types. As a trial the H$^+$ ion was exchanged with a metal ion such as X = Na$^+$, Li$^+$, K$^+$, Ca^{2+}, or Zn^{2+} through the ion-exchange membrane, where the PE samples with SO$_3$Na species were dipped in 2 N HCl aqueous solution for 50 h and then in X(OH)$_n$ aqueous solution for 14 days and dried at room temperature. For example, Figure 14 shows the FTIR spectra of the heavily sulfonated PE samples with the different metal ion species. The spectra are found to change largely depending on the metal ion species. One of the most significant changes is seen for the δ(OH) band in the 1600−1700 cm^{-1} region, indicating a different situation of the absorbed water surrounding the metal ion. The peak position and profile of the sulfonate bands are also different between the samples. For example, as the metal ion is changed from Li$^+$ to Na$^+$ to K$^+$, the peak position of the ν_s(SO$_3$) band tends to shift to the lower frequency side. This might originate from the difference in the atomic mass of the ions. However we cannot necessarily say so because the Ca^{2+} and Zn^{2+} ions give the band at a higher frequency position when compared with the case of the K$^+$ ion. Rather we should take into consideration not only the difference in the coordination structure made by the metal ion, sulfonate groups, and water molecules but also the different coupling between the π-conjugation structure and the sulfonate groups of the various metallic ions.

Qualitative Interpretation of the Characteristic Spectral Change for the Sulfonated Polyethylene Samples. As a general tendency the vibrational frequencies of the ν_{as}(SO$_3$) and ν_s(SO$_3$) modes have been said to be relatively close between R$-$SO$_3^-$ H$_3$O$^+$ and R$-$SO$_3^-$Na$^+$ for the low-molecular-weight compounds.[11,12] But, as described in the previous sections, the sulfonated PE samples with such a conjugation structure as C=C$-$C=C$-$SO$_3$X show clearly spectral changes depending on the degree of conjugation and on the different ion species. This means that the electronic or vibrational coupling between the SO$_3$X group and the skeletal chain is important in the sulfonated PE system.

The coupling between the S$-$O bond and the C=C conjugated bond has been discussed in detail from the viewpoint of molecular orbitals.[13−15] For example, Moffitt et al.[13,14] clarified that the π-character of the S$-$O bond becomes more significant when the contribution of the d orbital of the S atom is taken into consideration. If the ...C$-$C=C... conjugated chain is allowed to couple with the sulfonate group through the conjugation between the π-orbital of the carbon chain and the d-orbital of the S atom, then we may speculate the following mechanism for the high-frequency shift of the vibrational bands of ν_{as}(SO$_3$) and ν_s(SO$_3$). The π-orbital of the carbon atom and the d-orbital of the S atom are coupled, and some fraction of π-electron density of the carbon atom may flow into the S atom. Since the π-orbital of the O atom of the sulfonate group is originally coupled with the d-orbital of the S atom, then the flow-in of the π-electron of the C atom may induce the increase in the π-bond order of the S$-$O bonding of the sulfonate group. As a result of such an increase of the π-bond character, the force constant of the S$-$O bond may be increased and then the vibrational frequency may be increased. Such an enhancement of the electron flow from C=C to S$-$O through the coupling between the π- and d-orbitals may be more remarkable as the conjugated chain system is developed longer and longer. In this way, we may interpret qualitatively why the vibrational frequency of the S$-$O bond stretching is increased as the C=C conjugated system is developed. Unfortunately, however, this simple interpretation cannot give any reason for the different behaviors of the spectra for the SO$_3$H and SO$_3$Na species and also the other types of metallic ions. The sulfonate groups with different ion species might have different environments because of the different coordination structures of the SO$_3$ ion, the metallic ion, and water molecules. Such a different environment of the SO$_3$ groups may couple with the π-conjugation system in a different manner, resulting in the different spectroscopic behavior. A molecular orbital calculation might help us to clarify these situations more clearly.

References and Notes

(1) Ihata, J. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 167.
(2) Ihata, J. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 177.
(3) Ihata, J. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 187.
(4) Walles, W. E. U.S. Patent 3740258, 1971.
(5) Olsen, D. A.; Osteraas, A. J. *J. Polym. Sci., Polym. Chem. Ed.* **1969**, *7*, 1921.

(6) Walles, W. E. U.S. Patent 4220739, 1978.
(7) Lomonte, J. N. *Anal. Chem.* **1962**, *34*, 129.
(8) Schonk, R. M.; Bakker, B. H.; Cerfontain, H. *Recl. Trav. Chim. Pays-Bas* **1993**, *112*, 201.
(9) Heller, M. S.; Lorah, D. P.; Cox, C. G. *J. Chem. Eng. Data* **1983**, *28*, 134.
(10) Terentchev, A. P.; Domdrovskin, A. V. *Zh. Obshch. Khim.* **1951**, *21*, 704.
(11) Lin-Vien, D.; Colthup, N. B.; Fateley, W. G.; Grasselli, J. G. *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*; Academic Press, Inc.: New York, 1991.
(12) Detoni, S.; Hadzi, D. *Spectrochim. Acta* **1957**, *11*, 601.
(13) Moffitt, W. *Proc. R. Soc.* **1950**, *A200*, 409.
(14) Koch, H. P.; Moffitt, W. E. *Trans. Faraday Soc.* **1951**, *47*, 7.
(15) Santry, D. P.; Segal, G. A. *J. Chem. Phys.* **1967**, *47*, 158.

MA970062I