Bull. Chem. Soc. Jpn., 55, 2097—2100 (1982)

Fourier Transform Infrared Photoacoustic Spectroscopy of Polymers

Norio TERAMAE,* Masayuki HIROGUCHI, and Shigeyuki TANAKA
Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

(Received November 14, 1981)

Fourier transform infrared photoacoustic spectroscopy (FTIR-PAS) was applied to the structural elucidation of several kinds of organic polymers. By using a photoacoustic detection, infrared spectra of textile fabrics and rubbers containing carbon black could be measured without destructive and troublesome sample preparations. Curing process of resol type phenolic resins was examined by FTIR-PAS and conventional KBr disk method. FTIR-PAS was found to be sensitive to the structural change of the surface of the cured resins. Helmholtz resonance effect of the photoacoustic cell and the effect of the thermal properties of samples in FTIR-PAS were also discussed.

Photoacoustic spectroscopy (PAS) has been known to be a useful method for the analysis of bulk or rugged surface materials.[1)] Most of the studies on PAS, however, are limited to the uv-visible spectral region, for which powerful excitation sources are readily available. On the other hand, high power sources tunable over a wide spectral range do not presently exist in the infrared spectral region. In recent years, there has been a growing interest in PAS using Fourier transform infrared spectroscopy (FTIR),[2–11)] since a FTIR spectrometer has a greater throughput of radiation than the conventional dispersive infrared spectrometer.[12)] However, few discussions on the characteristics of the Fourier transform infrared photoacoustic spectroscopy (FTIR-PAS) have been made. In this study, some discussions on the factors which affect the FTIR-PAS spectra are made, and some application of FTIR-PAS to the structural elucidation of organic polymers is presented.

Experimental

The PAS system was composed of a home-made PAS attachment and a Digilab FTS-15 FTIR spectrometer.

Figure 1 shows a schematic drawing of the PAS cell employed in this study. The PAS cell was made of brass and its internal volume was approximately 0.95 cm^3. A KBr plate (3 mm thick) was used as a cell window and a 1/2 inch Bruel Kjaer 4165 condenser microphone was used as a pressure transducer. These were mounted on the PAS cell body by O-rings to ensure an air tight seal. Although KBr is one of the most transparent materials in the infrared region, it is susceptible to humidity. It should be noted that both highly transparent and wet-proof windows can not be available in the infrared region, and that the Helmholtz resonance effect affects the FTIR-PAS spectra as will be mentioned later. Therefore, the cell was designed so that the windows could be replaced easily and also that the volume in front of the microphone diaphragm could be adjusted easily in order to obtain optimum efficiency.

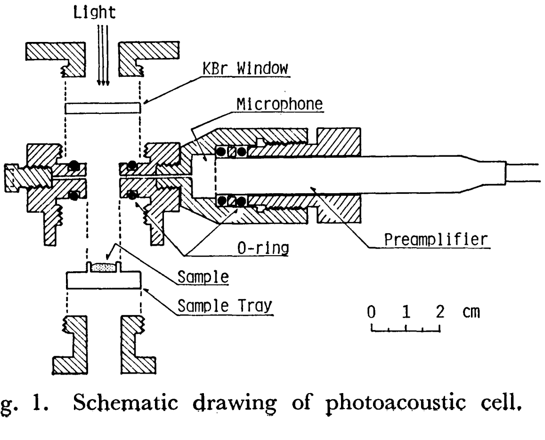

Fig. 1. Schematic drawing of photoacoustic cell.

The photoacoustic signals from the microphone attached to the PAS cell were amplified with a Brookdeal 9454 a.c. amplifier and were fed to the HgCdTe detector amplifier section of the FTIR spectrometer. All of the spectra were measured at 4 cm^{-1} resolution using 900 scans which took about 25 min.

Results and Discussion

Characteristics of FTIR-PAS. Figure 2 shows the photoacoustic spectrum of carbon black (benzene soot) and the source spectrum measured by a triglycine sulfate (TGS) detector. The carbon black PAS spectrum and the source spectrum measured by a pyroelectric detector such as TGS are known to be vir-

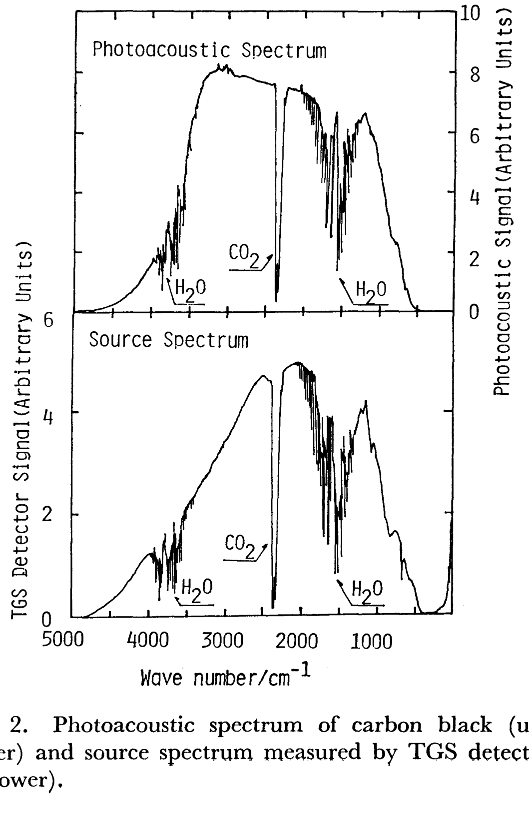

Fig. 2. Photoacoustic spectrum of carbon black (upper) and source spectrum measured by TGS detector (lower).

tually identical with each other in the dispersive PAS system with a fixed frequency light modulation.[13,14] As shown in Fig. 2, the above identity is not observed in the case of FTIR-PAS. This result can be considered to be attributed to the difference of the light modulation methods between the interferometry and the dispersive spectrometry. In the case of rapid scanning FTIR, the frequency of the radiation being emitted from the source, ν[cm^{-1}], corresponds to the modulation frequency, ω[s^{-1}], through the relationship, $\omega=2V\nu$, where V represents the velocity of the moving mirror in a Michelson interferometer.[12] Considering that the carbon black PAS signals are inversely proportional to the modulation frequencies,[15] carbon black PAS signals for FTIR-PAS must be larger in the lower wave number region. However, this expected tendency was not observed as shown in Fig. 2. Accordingly, another additional effect must be taken into consideration for the analysis of FTIR-PAS spectra. Since another type of PAS cell[2] showed a different spectral pattern of carbon black compared with the results shown in Fig. 2, the possibility of the influence of the Helmholtz resonance effect was examined by changing the volume in front of the microphone diaphragm.

The Helmholtz resonance frequency, ω_0, is given by[16]

$$\omega_0 = (v_0/2\pi)[\{(1/V_1)+(1/V_2)\}\sigma/\{L+(1/2)(\pi\sigma)^{1/2}\}]^{1/2},$$

where v_0 is the speed of sound, and V_1 and V_2 are the volume of the sample cavity and the volume in front of the microphone diaphragm, respectively. σ is the cross-sectional area of the tube of length L connecting the volume V_1 and V_2. Figure 3 shows the photoacoustic spectral changes due to the Helmholtz resonance effect when V_2 is changed from 90 to 750 mm^3. These curves were obtained by dividing the carbon black PAS spectra by the source spectrum presented in Fig. 2. As shown in Fig. 3, the peak which represents resonance frequency moves to lower wave numbers, as the volume V_2 becomes larger. The observed resonance frequencies were plotted against the $[(1/V_1)+(1/V_2)]^{1/2}$ values, and a good linear correlation was obtained as shown in Fig. 4. From the above-mentioned fact, the PAS signals in FTIR are considered to be influenced greatly by the Helmholtz resonance effect. Strictly speaking, the effect of the volume of sample must be taken into consideration for the normalization of FTIR-PAS spectra. However, the effect can be neglected if V_1 is sufficiently greater than V_2.

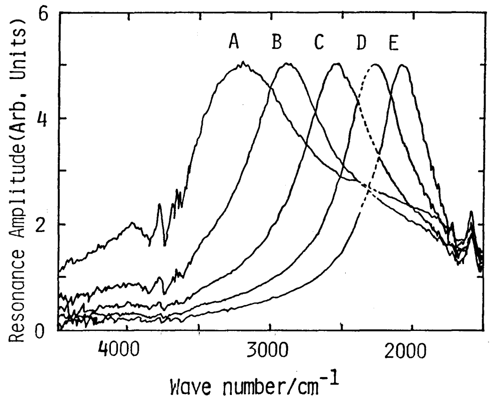

Fig. 3. Resonance effect obtained by changing the volume in front of the microphone diaphragm.
The volumes, V_2, are 90(A), 150(B), 290(C), 420(D), and 750(E) in mm^3 units.

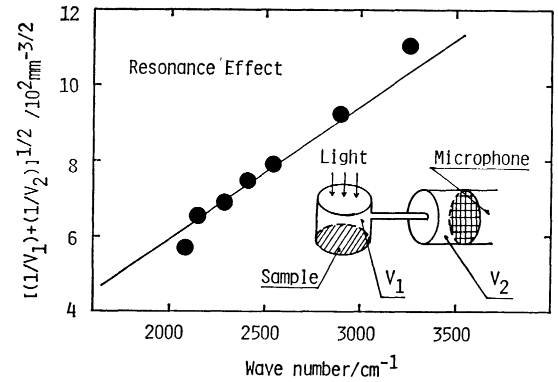

Fig. 4. Helmholtz resonance effect of the photoacoustic cell.

Although the above effect can be compensated when the normalization of the sample PAS spectra is carried out by using a carbon black PAS spectrum measured by the same PAS cell as a reference, the effect must be taken into account if the measurement of FTIR-PAS is carried out by the use of double beam measurement system which requires two PAS cells. Of cource, if a completely non-resonant type of PAS cell is used, the above-mentioned effect can be neglected. However, it is considered to be better to use a resonant type of PAS cell in order to improve the S/N ratio of PAS spectra, since the usual light source in the infrared spectral region is not powerful.

FTIR-PAS spectra of several kinds of polymers such as cloths, rubbers, cured resins *etc.* were measured. Although the features of these spectra were fairly similar to those of published spectra measured by a KBr method or an ATR method etc., photoacoustic signals were found to be larger in the lower wave number regions. This result can be attributed to the thermal properties of the samples, since the thermal diffusion length in the sample depends on the modulation frequency.[15] The samples investigated in this study are considered to be optically opaque and thermally thick solids, for which photoacoustic signals show $\omega^{-3/2}$ dependence, where ω is the modulation frequency. In this case, further normalization must be carried out by multiplying a factor of $\omega^{1/2}$, that is $(2V\nu)^{1/2}$, after simply dividing the raw PAS spectrum by a carbon black PAS spectrum, since carbon black PAS signals are inversely proportional to ω. The above mentioned normalizing procedures would be necessary if we wish to compare the PAS spectra with the standard spectral data such as IRDC cards.

FTIR-PAS Spectra of Polymers. Figure 5 shows the PAS spectra of nylon cloth and cotton cloth. The features of these spectra are fairly similar to those of the published spectra measured by a KBr method or a thermally pressed film method.[17] Using the photoacoustic detection, infrared spectra of these textile fabrics can be obtained by simply putting a small piece of sample into the PAS cell. Thus, it can be said that FTIR-PAS could be a simple but still effective method for the identification of these compounds without troublesome and destructive sample preparations which are nescessary for conventional measurement techniques.

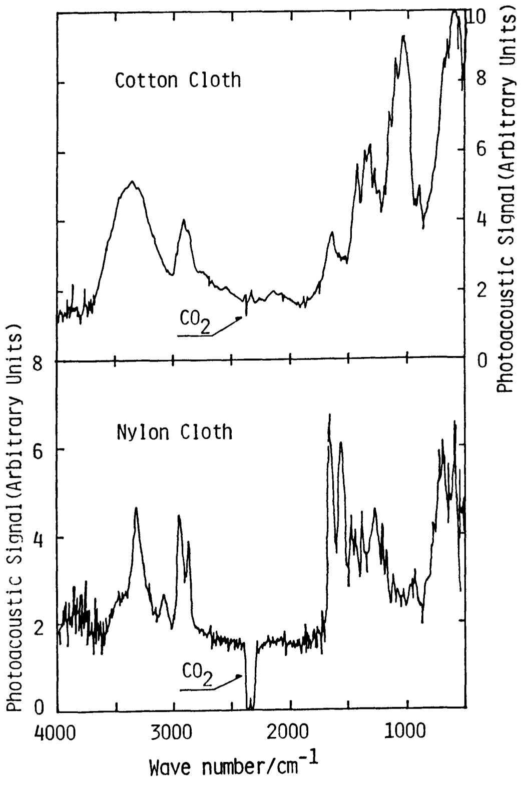

Fig. 5. Photoacoustic spectra of cotton (upper) and Nylon (lower) cloths.

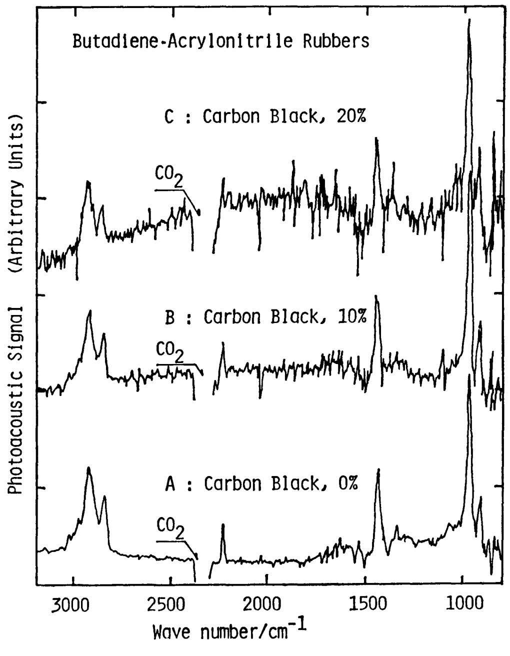

Fig. 6. Photoacoustic spectra of butadiene-acrylonitrile rubbers containing carbon black.
Carbon black content, A: 0%, B: 10%, C: 20%.

In Fig. 6, PAS spectra at the top, the middle and the bottom show butadiene–acrylonitrile rubbers containing carbon black, 20, 10, and 0%, respectively. Commercial rubbers usually contain carbon black or silica in order to enhance elasticity. The conventional measurement technique used to examine rubbers is an ATR method, which requires a specially designed apparatus,[18] capable of taking a large incident angle for obtaining spectra of the sample containing carbon black because of the high refractive indices of samples. As shown in Fig. 6, however, structural elucidation of rubbers can be made in the same manner regardless of the content of carbon black in the range of 0 to 20%. It can be seen that the S/N ratio of the PAS spectra decreases as the content of carbon black increases. This result is possibly due to the fact that the more carbon black a sample contains, the less light it receives. From the fact, FTIR-PAS would be more useful for the structural elucidation of rubbers which contain silica, since silica absorbs less light than carbon black does.

Figure 7 shows the spectral change by curing a resol type phenolic resin. These spectra were measured after heating the sample at 170 °C for 0, 15, 30, 60, and 120 min. The curing process of the resin was reported to be characterized as follows.[19] As the resin is heated, the intensity of the band due to C–O–C stretching vibrational mode at about 1050 cm^{-1} decreases, and a new band due to carbonyl stretching vibrational mode at about 1650 cm^{-1} appears. The new band is considered to be caused by the oxidation of the methylene group. The PAS spectral changes are well consistent with the above proposed curing process. In Fig. 8, spectra at the left and the right halves are the expanded spectra of the above-

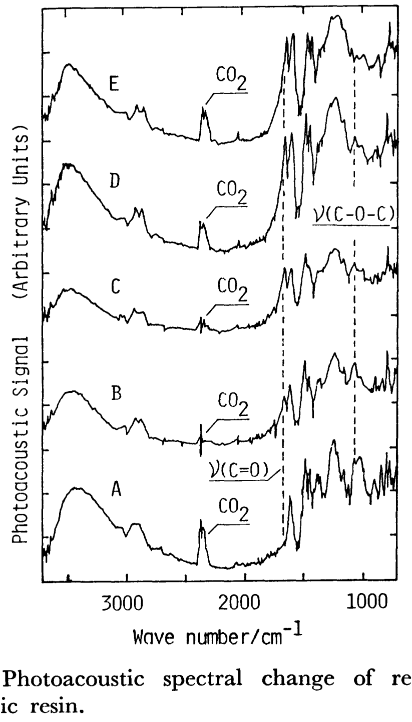

Fig. 7. Photoacoustic spectral change of resol type phenolic resin.
Heating temperature is 170 °C. Heating periods are 0(A), 15(B), 30(C), 60(D), and 120(E) min.

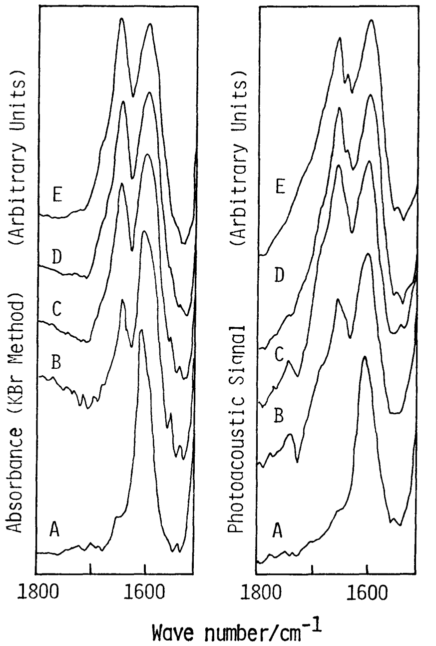

Fig. 8. Absorption spectra measured by a KBr method (left side) and photoacoustic spectra (right side) of cured resol type phenolic resins.
Heating periods are 0(A), 15(B), 30(C), 60(D), and 120(E) min.

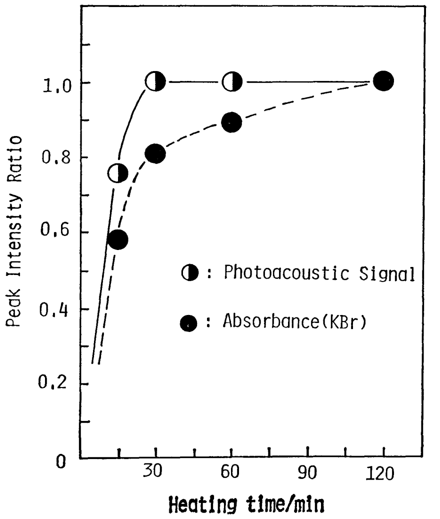

Fig. 9. Peak intensity ratio of the 1650 cm^{-1} band to the 1610 cm^{-1} band *vs.* heating time.

mentioned resins measured by absorption and photoacoustic techniques, respectively. The absorption spectra were obtained by a KBr method, in which the resins used for measuring FTIR-PAS were ground to fine powders. During the curing of resol type phenolic resins, the absorption intensity of the band at about 1610 cm^{-1} which is assigned to aromatic C=C stretching vibrational mode is said to be unchanged.[19] Therefore, in order to examine the degree of curing of the resin as well as to compare results which is obtained by the two measuring methods presented in Fig. 8, the ratio of the intensity of the carbonyl absorption band at 1650 cm^{-1} to that of the aromatic absorption band at 1610 cm^{-1} was plotted against the heating period by using absorption and photoacoustic spectra. The results are shown in Fig. 9. Comparing the two curves in Fig. 9, it is immediately seen that the ratio reaches to a constant value within 30 min by using the PAS spectral data. Whereas, as for the absorption spectral data, the ratio is gradually increases as the heating time increases. This result reflects that the PAS is sensitive to the structural change of the surface of cured resin, and that averaged information about the mixed species of cured and non-cured resins is obtained by the absorption method such as a KBr technique. If the constant value in the ratio shown in Fig. 9 is caused by the saturation effect of the photoacoustic signal,[15] the depth of the cured layer can be estimated. Assuming that the thermal diffusivity of the cured resin is 0.001 (cm^2/s), thermal diffusion length of 5.7 microns is obtained at 1650 cm^{-1} under the measuring conditions in our spectrometer.[3] Accordingly, the cured layer of several microns can be considered to be formed during the heating of 0 to 30 min. Thus, FTIR-PAS is useful for the surface characterization of cured resins. In some cases, cured resins are difficult to examine by conventional measurement techniques because of their mechanical hardness. For the analysis of such materials, FTIR-PAS is also effective, since FTIR-PAS requires minimal sample preparations.

The authors wish to express their thanks to Dr. Tsuguo Sawada and Professor Yohichi Goshi, The University of Tokyo, and Dr. Shohei Oda, Fuji Film Co., Ltd., for their helpful discussions. We also would like to thank Dr. Morio Tsuge, Sumitomo Bakelite Co., Ltd., for providing phenolic resins as samples.

References

1) A. Rosencwaig, *Anal. Chem.*, **47**, 592A (1975).
2) N. Teramae and S. Tanaka, *Spectrosc. Lett.*, **14**, 687 (1981).
3) N. Teramae, M. Hiroguchi, and S. Tanaka, *Chem. Lett.*, **1981**, 1091.
4) N. Teramae, T. Yamamoto, M. Hiroguchi, T. Matsui, and S. Tanaka, *Chem. Lett.*, **1982**, 37.
5) M. G. Rockley, *Chem. Phys. Lett.*, **68**, 455 (1979).
6) D. W. Vidrine, *Appl. Spectrosc.*, **34**, 314 (1980).
7) M. G. Rockley, D. M. Davis, and H. H. Richardson, *Science*, **210**, 918 (1980).
8) M. G. Rockley and J. P. Devlin, *Appl. Spectrosc.*, **34**, 407 (1980).
9) M. G. Rockley, *Appl. Spectrosc.*, **34**, 405 (1980).
10) G. Laufer, J. T. Huneke, B. S. H. Royce, and Y. C. Teng, *Appl. Phys. Lett.*, **37**, 517 (1980).
11) M. G. Rockley, *Chem. Phys. Lett.*, **75**, 370 (1980).
12) P. R. Griffiths, "Chemical Infrared Fourier Transform Spectroscopy," John Wiley & Sons, New York (1975).
13) W. R. Harshbarger and M. B. Robin, *Acc. Chem. Res.*, **6**, 329 (1973).
14) R. G. Gray, V. A. Fishman, and A. J. Bard, *Anal. Chem.*, **49**, 697 (1976).
15) A. Rosencwaig and A. Gersho, *J. Appl. Phys.*, **47**, 64 (1976).
16) N. C. Fernelius, *Appl. Opt.*, **18**, 1784 (1979).
17) D. O. Hummel, "Atlas der Kunstsoff-Analyse," Verlag Chemie (1968).
18) S. Tanaka and T. Matsui, *Bunseki Kagaku*, **20**, 1128 (1971).
19) M. Yamao, S. Nukui, and S. Tanaka, *Nippon Kagaku Kaishi*, **1972**, 914.