and the aqueous phase can be seen from fluorescence measurements. However, a quantitative estimate of the solvent fraction in the polymer phase is difficult. The kinetics of solvent partitioning in the systems investigated is fast and is of the magnitude expected from the diffusion equation.

Registry No. DEGBA, 31353-26-1; DEGEE, 111-90-0; (butyl methacrylate)(butyl acrylate)(methacrylic acid) (copolymer), 30231-49-3.

References and Notes

(1) Dale, R. E.; Chen, L. A.; Brand, L. *J. Biol. Chem.* **1977**, *252*, 7500.
(2) Lakowicz, J. R.; Prendergast, F. G.; Hogen, D. *Biochemistry* **1979**, *18*, 520.
(3) Prendergast, F. G.; Haugland, R. P.; Callahan, P. J. *Biochemistry* **1981**, *20*, 7333.
(4) Engel, L. W.; Prendergast, F. G. *Biochemistry* **1981**, *20*, 7338.
(5) Stubbs, C. D.; Kinosita, K., Jr.; Munkonge, F.; Quinn, P. J.; Ikegami, A. *Biochem. Biophys. Acta* **1984**, *775*, 374.
(6) Cundall, R. B.; Johnson, I.; Jones, M. W.; Thomas, E. W.; Munro, I. H. *Chem. Phys. Lett.* **1979**, *64*, 39.
(7) McGlade, M. J.; Randall, F. J.; Tcheurekdjian, N. *Macromolecules* **1987**, *20*, 1782.
(8) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Plenum: New York, 1986.
(9) Popli, R.; Luccas, M. H.; Tsaur, S. L., manuscript in preparation.
(10) Popli, R.; Luccas, M. H. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1988**, *29* (June), 458.

On the Sensitivity of Photoacoustic Fourier Transform Infrared Spectroscopy to Cross-Linking Reactions

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Network formation, such as occurs during the curing of elastomers or thermosets, is a complex process that often forcloses the use of many analytical techniques to gain an understanding of the molecular architectures that develop. Since the measurements of macroscopic properties do not provide adequate information, one could propose at least a few spectroscopic methods to monitor the polymer network formation. However, the experimental difficulties or sensitivity may impose various limitations. In this contest, Fourier transform infrared (FT-IR) spectroscopy is no exception. Although we have a considerable interest in the development of this technique since it is a probe on a molecular level, the experimental difficulties in using it to evaluate the events during polymer network formation may cause some problems. While useful theoretical approaches (Gordon,[1] Mark,[2] Macosko,[3] and Eichinger[4]) have been developed, it is apparent that very little experimental work utilizing FT-IR was reported. Actually, this is not surprising if one analyzes the spectral changes that occur during the cross-linking process of hydroxyl-terminated poly(dimethylsiloxane) (PDMS, MW = 18000, Petrarch) with tetraethoxysilane (TES, Petrarch; catalyst, tin octoate). As seen in Figure 1, neither the intensity changes nor the appearance or disappearance of bands during various stages of curing is being observed. At this point it is necessary to raise the question as to why the cross-linking process cannot be detected by transmission measurements while the technique provides an adequate sensitivity to detect, for example, a compatibility of polymer

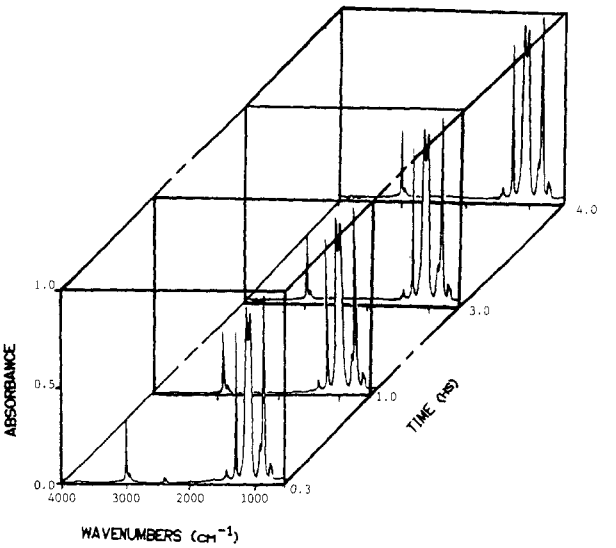

Figure 1. Transmission FT-IR spectra of PDMS/TES recorded at various stages of curing.

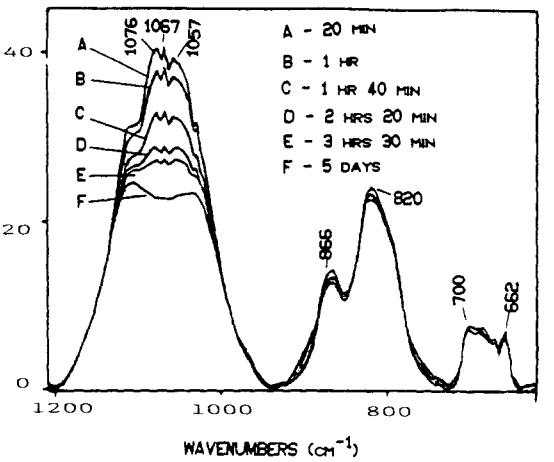

Figure 2. Photoacoustic FT-IR spectra of PDMS/TES recorded at various stages of curing.

blends.[5,6] One of the essential problems in cross-linking reactions is a small number of cross-links compared to the number of other bonds in the system. In addition, during the cross-linking of this particular system, the Si–OH bonds of PDMS and H_5C_2–O–Si of TES break to form the Si–O–Si network and ethanol. Thus, the simultaneous cleavage and formation of energetically similar bonds result in a heavy spectral overlap of strongly absorbing bands. Although one could monitor the disappearance of hydroxyl bands, their content is molecular weight dependent and, even with the relatively low molecular weights, their detection becomes impossible. Hence, in spite of the high sensitivity and speed of transmission FT-IR, this technique has an Achilles heel.

Let us examine the same cross-linking reaction by photoacoustic FT-IR spectroscopy. While the transmission FT-IR measurements do not provide sufficient sensitivity, the situation changes drastically when the same process is monitored photoacoustically. Figure 2 illustrates the spectral region from 1210 to 625 cm^{-1} recorded as a function of time. It is clearly seen that the band at 1067 cm^{-1}, as well as other bands in the spectra, diminishes in intensity with time. On the other hand, the bands at 662 and 700 cm^{-1} remain virtually unchanged as the reaction progresses. In order to provide a semiquantitative picture of the curing process, it is appropriate to compare the photoacoustic and transmission intensity changes plotted

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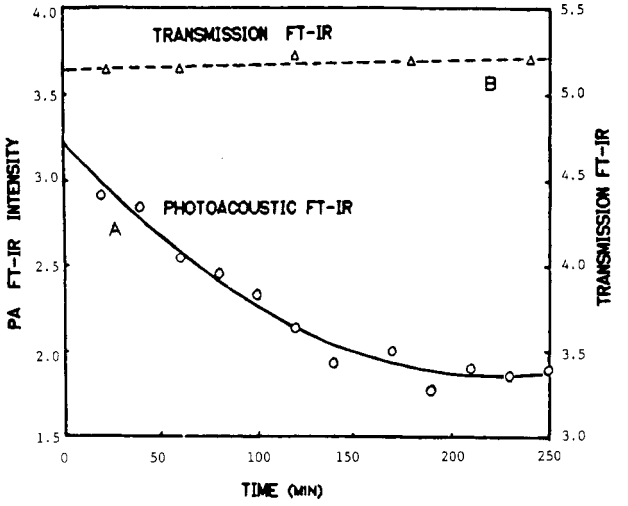

Figure 3. Intensity ratio of the 2962- and 700-cm^{-1} bands plotted as a function of time: (A) photoacoustic FT-IR detection; (B) transmission FT-IR.

as a function of time. This shown in Figure 3. It is noted immediately that at any time of the reaction, the infrared intensities recorded in the transmission mode remain unchanged. On the other hand, the photoacoustic detection shows drastic changes, in particular at the early stages of curing.

At this point it is necessary to reveal the origin of the spectral changes in photoacoustic detection and correlate this information with the processes that occur during network formation. In an effort to do so we have taken two approaches. First, since ethanol is produced during the reaction, the decreasing intensities may be related to the escape of ethanol from the system. Second, as the cross-linked network is being formed, the thermal properties of the system (heat capacity, thermal conductivity) may also change. However, the latter would be reflected in the intensity changes of all photoacoustically detected bands because the photoacoustic spectrum is not only a spectroscopic method but also a calorimetric method to measure the amount of electromagnetic radiation converted to heat.[7,8] Because only selected infrared bands are effected by the cross-linking reactions, it seems that the property changes may play some role but they are not fully responsible for the observed intensity changes. As a matter of fact, examination of the intensity changes depicted in Figure 2 indicates that the bands that decrease during the reaction correspond to the ethanol bands. Thus, it is believed that the observed changes are attributed to the removal of ethanol from the reaction mixture. Similar features were found in the OH and CH stretching regions of the spectra and are also attributed to the ethanol bands. Although we hoped that the changes of thermal conductivity or heat capacity during curing of PDMS will effect the intensity of the photoacoustic signal, at this point there is no experimental evidence as such. It should be mentioned that the material property changes upon curing would influence the thermal diffusion length[8] and, therefore, the intensity of entire photoacoustic spectrum, not only selected bands. This is governed by the following equation:

$$\mu_{th} = (2\alpha/\omega)^{1/2}$$

where μ_{th} is the thermal diffusion length, α is the thermal diffusivity ($\alpha = k/\rho C$; k, thermal conductivity; ρ, density; C, heat capacity), and ω is the modulation frequency. A vinyl-terminated PDMS will be a suitable system to test the above hypothesis since no byproducts are released

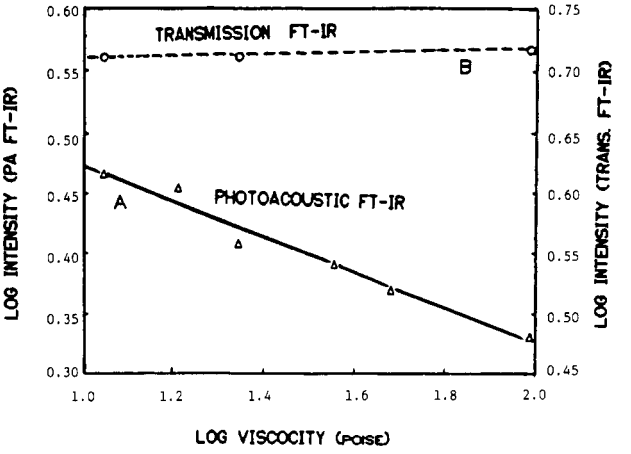

Figure 4. log intensity ratio (from Figure 3) plotted as a function of log viscosity during the curing process of the PDMS/TES system: (A) photoacoustic FT-IR detection; (B) transmission FT-IR.

during its cross-linking (future work).

While a detailed analysis of the spectral changes presented above will be the subject of our future work, here we only point out the usefulness of these measurements by correlating the intensity changes with the viscosity data, also recorded as a function of time. A log–log plot, shown in Figure 4A, indicates that indeed a linear correlation exists, suggesting that the production of ethanol during the cross-linking process is proportional to the extent of cross-linking. For comparison purposes the same plot was constructed based on the transmission measurements (Figure 4B). Apparently, the viscosity increase has no effect on the infrared band intensities recorded in this mode.

In summary, the commonly employed technique for the surface studies,[9-11] photoacoustic FT-IR spectroscopy, may be a useful tool in monitoring the network formation of the systems in which transmission FT-IR cannot provide sufficient sensitivity. These preliminary studies show that it is possible to monitor spectroscopically the end-linking reactions of elastomers and correlate the photoacoustically detected intensity changes with the viscosity measurements. To our knowledge, the presented data demonstrate the first spectroscopic evidence for monitoring such reactions by FT-IR.

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Registry No. Tetraethoxysilane, 78-10-4.

References and Notes

(1) Gordon, M.; Ward, T. C.; Whitney, R. S. In *Polymer Networks*; Chompf, A. J., Newman, S., Eds.; Plenum: New York, 1971.
(2) Mark, J. E.; DeBolt, L. C. *Macromolecules* **1987**, *20*, 2369.
(3) Miller, D. R.; Valles, E. M.; Macoscko, C. W. *Polym. Eng. Sci.* **1979**, *19*(4), 272.
(4) Leung, Y. K.; Eichinger, B. E. *J. Chem. Phys.* **1984**, *80*(8), 3877.
(5) Lee, J. Y.; Painter, P. C.; Coleman, M. M. *Macromolecules* **1988**, *21*, 346.
(6) Coleman, M. M.; Painter, P. C. *Appl. Spectrosc. Rev.* **1984**, *20*, 255.
(7) Urban, M. W. *J. Coat. Technol.* **1987**, *59*, 29 and references therein.
(8) Rosencwaig, A. *Photoacoustics and Photoacoustic Spectroscopy*; Wiley: New York, 1980; and references therein.
(9) Urban, M. W.; Salazar-Rojas, E. M. *Macromolecules* **1988**, *21*, 372.
(10) Urban, M. W.; Koenig, J. L. *Appl. Spectrosc.* **1986**, *40*(6), 851.
(11) Urban, M. W.; Koenig, J. L. *Appl. Spectrosc.* **1986**, *40*(7), 994.