

Effect of Catalyst Residues on the Degradation of Rigid Foam Polyurethane

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Synopsis

Immediately after heating rigid foam polyurethane (PU) at 165°C, it degrades in accordance with the degradation mechanisms suggested by Abu-Zeid et al. in earlier publications. However, after three days all photoacoustic spectra (PAS) bands indicative of PU degradation almost disappeared, and the samples were found to resist both UV and thermal degradation for a wide range of temperatures and UV dosages. Residual catalysts left from PU polymerization were found to be the main cause of its degradation. When these residues were consumed in the process of solid repolymerization, PU becomes immune to heat and UV degradation.

INTRODUCTION

Rigid foam polyurethane is widely used as a thermal insulator. Study of thermal degradation of polyurethane using photoacoustic spectroscopy¹⁻³ (PAS) revealed that degradation can occur at a relatively low temperature (60°C). Abu-Zeid et al.^{2,3} reported that polyurethane degradation is due to free radicals and it continues for a long time. They also reported that at a certain temperature the PAS band between 190 and 200 nm decreases and then eventually disappears with increased storing time while the PAS bands between 220 and 270 nm and 270 and 320 nm, due to aromatic amines or urea, remain unchanged. No explanation was given for this observation at that time. In this article we will examine, in detail, this phenomena.

EXPERIMENTAL

Photoacoustic Spectrometer

The photoacoustic spectrometer used in this study was described in detail in previous publications.⁴⁻⁹ A stainless steel sample holder which accepts a 5 × 8 × 2 mm sample was used. Air was used as a coupling medium between the sample and the microphone. The exit slit of the scanning monochromator was 2 mm at which the resolution of the monochromator is 8 nm. Carbon black was used as a reference (*R*) against which all the spectra were normalized.

Samples and Sample Preparation

Polyurethane rigid foam formed by the reaction of 1,4-butane diol and methyl-bis(4-phenyl-diisocyanate) was used in this work. Identical 5 × 8 × 2 mm samples were prepared and kept in a light-tight box. The samples

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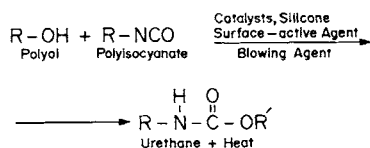
were heated in a calibrated oven at temperatures of 150, 155, 160, 165, 170, and 180°C for 15 min and kept also in a light-tight container for analysis. In all figures $(S-B)/R$ is plotted against the wavelength, where S is the PAS of the treated sample, B is the PAS of identical but nontreated sample, and R is the PAS of the reference (carbon black). In this way $(S-B)/R$ gives the net change that might take place during the degradation. Each recorded spectrum is the average of the PAS spectra of three samples prepared in the same way and subjected to the same conditions to ensure a good representation of the data we obtained.

UV Irradiation

Spectra physics CW Ar Ion Laser Model 171A was used for UV irradiation at 335 nm wavelength and 0.5 W power. The samples were irradiated for different times. The laser beam covers the whole area of the samples surface.

RESULTS AND DISCUSSION

The rigid foam polyurethanes used in this article are prepared according to Scheme I¹⁰:



The catalysts used were tertiary amines or organic salts of divalent tin which activate isocyanate. Both silicon surface active agent and the blowing agents are also participating in the above reaction. A temperature between 100 and 170°C could be reached in the center of the foam during the solidification of the mass and the cessation of the expansion. In general, catalysts are used in certain production stages of all commercially produced polyurethane. It was found also that certain basic impurities can act as "catalysts."

Whether catalysts are impurities or specific ingredients, if they are not totally consumed during the polymerization process, the residues left behind in the polymer could act as nuclei for polymer degradation. If, however, polymer containing these traces degraded to its main ingredients through which it was originally formed, and if the temperature of the mixture happens to be the right temperature for the catalysts to initiate the reaction between polymer constituents, the original polymer will be reformed. This could take place in both solid and liquid phase of the polymer's constituents.

Many polymers are capable of polymerizing not only in liquid phase but also in solid phase below their melting points.¹² This mechanism of polymerization, which is usually initiated by high energy particles or ionizing radiation, is known as solid-phase polymerization. It is also well known that, near the solid polymer melting point, polymerization of solid monomer increases sharply and often turns out to have a higher rate of polymerization than exhibited by the same monomer in the liquid phase at a considerably

higher temperatures.¹² It seems that solid-phase polymerization also occurs with the aid of the catalyst residues under a suitable temperature as evidence from the data we obtained.

Figure 1 shows the PAS spectra of a rigid foam polyurethane (formed according to Scheme I) heated for 15 min at 150, 155, 160, 165, 170, and 180°C. All spectra were recorded 1 day after the samples were heated. Two bands appeared in the PAS spectra, one band is between ≈ 220 and 270 nm and the other is between ≈ 270 and 320 nm with extended tail to 450 nm. One striking observation in Figure 1 is the dependence of the PAS intensity on the temperature of heating. The sample kept at 165°C shows the least intensive spectrum compared to the spectra obtained from the samples kept at higher as well as lower temperatures than 165°C.

In Figure 2 we followed the development of the PAS spectra of the sample heated at 165°C with the storing time. Immediately after heating the sample at 165°C, the sample followed the normal behavior of the degradation pattern reported earlier.² After that the intensity of the band between 220 and 270 nm, which is due to $\pi-\pi^*$ transition of aromatic amines or urea, starts to decrease with time. It reaches its lowest and stable value after 3 days. However, the band between 270 and 320 nm, which is due to $n-\pi^*$ transition of aromatic amine, aromatic urea, and the base material of polyurethane methylene bis(4-phenyl diisocyanate) (MBPI), did not change

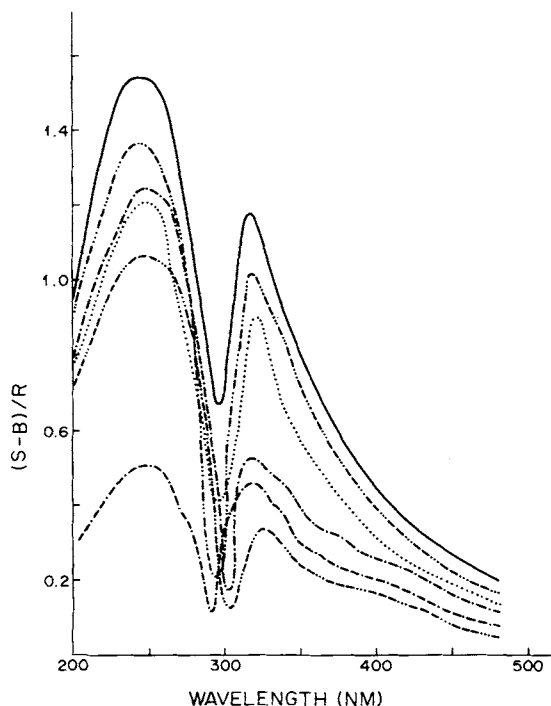


Fig. 1. Photoacoustic spectra of rigid foam polyurethane samples heated for 15 min at: (— · · · —) 150°C; (—) 155°C; (· · ·) 160°C; (— · · —) 165°C; (— · · · ·) 170°C ($\times 0.5$); (— · —) 180°C ($\times 0.5$). All PAS spectra were recorded 1 day after the samples were heated.

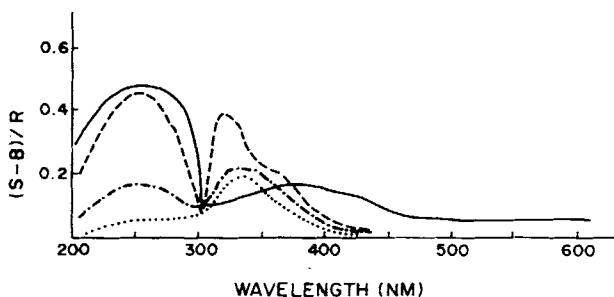
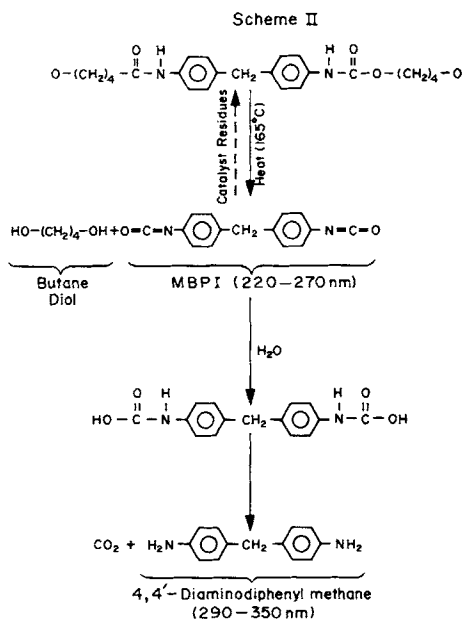


Fig. 2. PAS spectra of the rigid foam polyurethane sample heated for 15 min at 165°C after storing it for the periods: (—) 3 h; (---) 1 day; (- · -) 2 days (···) 3 days.

appreciably. The apparent decrease in the intensity of this band with storing time is perhaps due to the contribution of the long wavelength tail of the band between 220 and 270 nm. This contribution is therefore larger for the spectra obtained at shorter storing time. It was found that, after storing the sample for 3 days or longer, the PAS band due to MBPI almost disappears. This experiment has been repeated several times, and the reproducibility of the above data have been confirmed without any doubt.

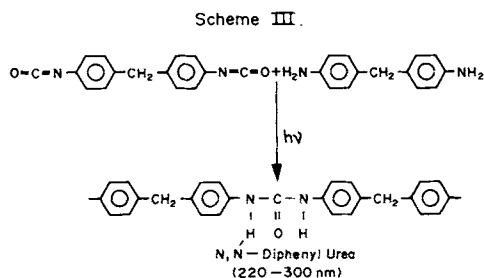
The question now is what happened to MBPI formed immediately after the sample exposed to 165°C for 15 min? To answer this question, one has to examine what happens to polyurethane heated at 165°C. The mechanism of degradation of polyurethane at this temperature is illustrated by solid arrows in the mechanistic Scheme II²:



If however, there are residual traces of catalysts that are not fully consumed in the initial process of polymerization and 165°C happens to be the right temperature for these residual catalysts to initiate solid phase polymerization between butane diol and MBPI, one can easily explain the data of

Figure 2. Once MBPI is formed two competing processes take place. One process deals with the reformation of polyurethane from butane diol and MBPI with the help of the residual catalysts. The second process involves the formation of 4,4-diaminodiphenyl methane through the reaction of MBPI with the moisture of water from the atmosphere. It is clear that both processes cooperate in effecting a nearly complete disappearance of the band between 220 and 270 nm.

A further interesting observation is shown in Figure 3. In this figure the sample previously heated at 165°C for 15 min and stored for 3 days was then reheated to 100°C and its spectra were recorded at different storing periods. After 1 day, a weak band between 290 and 350 nm appeared. This weak band is due to the formation of 4,4'-diaminodiphenylmethane according to Scheme II. After 7 days, however, this weak band disappeared due to the formation of *N,N*-diphenyl urea according to Scheme III:



The presence of catalyst residues in the polyurethane act as impurity centers which could initiate its degradation. The traces of residual catalysts left behind after heating polyurethane to 165°C and not used in its re-polymerization were apparently too small to cause any appreciable degradation at any temperature < 165°C.

Figure 4, however, shows the PAS spectra of the previously heated sample (at 165°C for 15 min and stored for 3 days) when reheated to 200°C. All the bands due to polyurethane degradation appeared once more, and the sample became no longer immune to heat degradation. This is clearly understood since a 200°C is a relatively harsh temperature for polyurethane and causes brownish coloration of the sample. At this temperature atmospheric O₂ is sufficient for initiating oxidative degradation² with the formation of quinonimide which gives rise to a PAS absorption band between 400 and 550 nm.

A last interesting observation is that shown in Figure 5. In this figure the sample previously heated at 165°C for 15 min and stored for 3 days was subjected to a certain UV irradiation dose, and then its PAS spectra were recorded at different storing times. The PAS band due to 4,4-diaminodiphenyl-methane disappeared and instead a weak band between 220 and 300 nm starts to develop with the storing time. This band is due to the reaction of the traces of MBPI (that are not converted to polyurethane or diamine in the mechanistic Scheme II) with the diamine to form diphenyl urea which has a peak around 265 nm with extended tail to 300 nm as per Scheme III. The disappearance of the band due to diamine indicates that indeed this compound exists in the sample before its UV irradiation but in

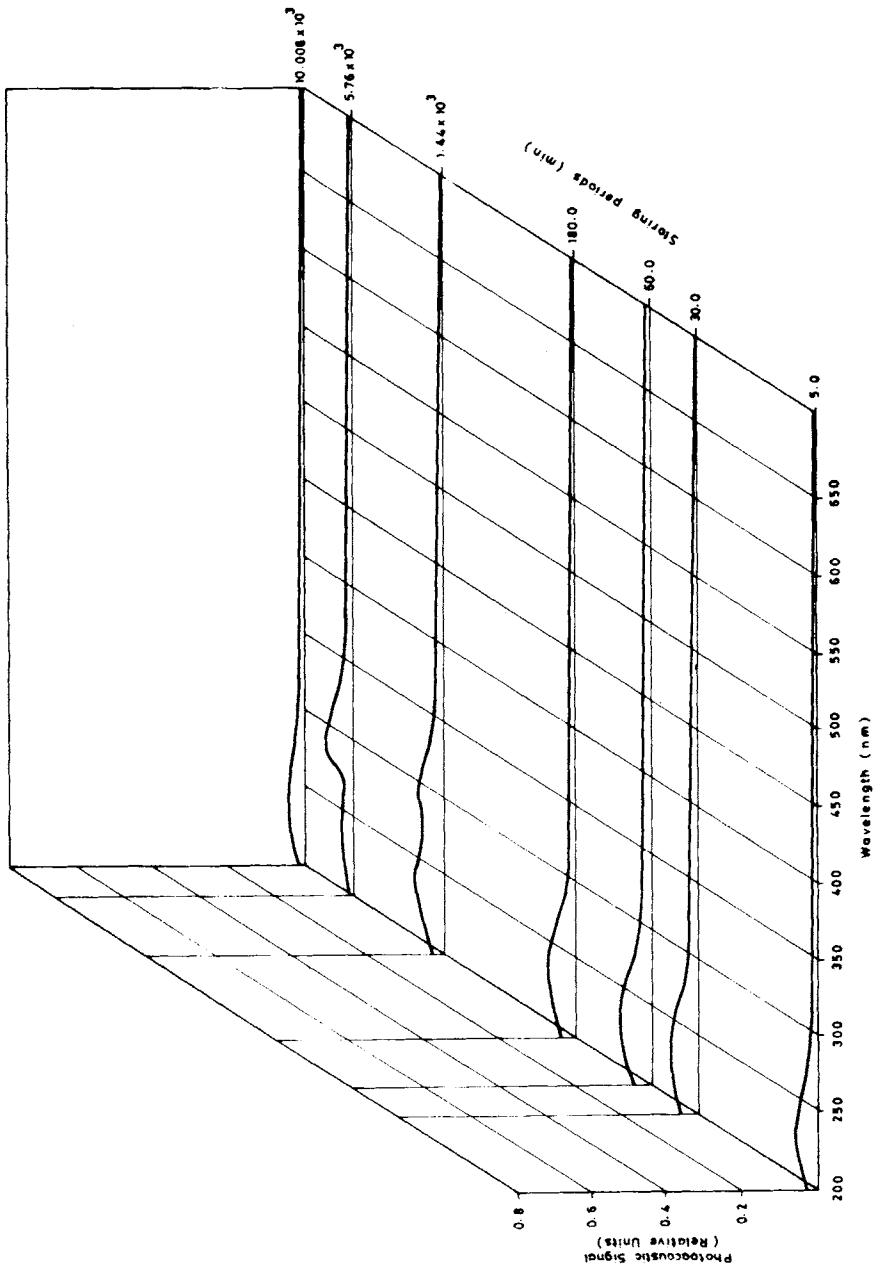


Fig. 3. PAS spectra of the rigid foam polyurethane sample previously heated at 165°C for 15 min and stored for 3 days. The sample was then reheated at 100°C for 15 min and stored for the periods indicated on the figure.

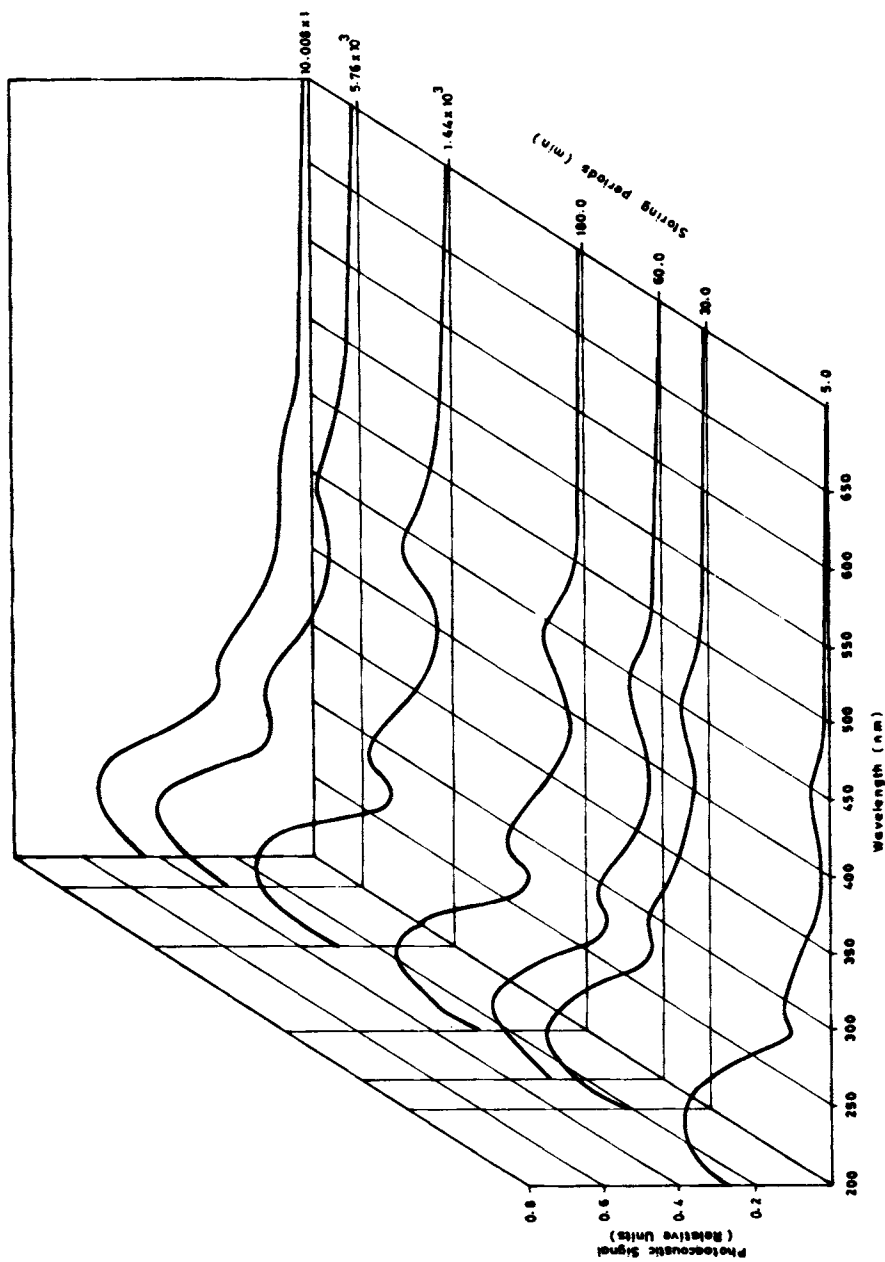


Fig. 4. PAS spectra of the rigid foam polyurethane sample previously heated at 165°C for 15 min and stored for 3 days. The sample was then reheated at 200°C for 15 min and stored for the periods indicated on the figure.

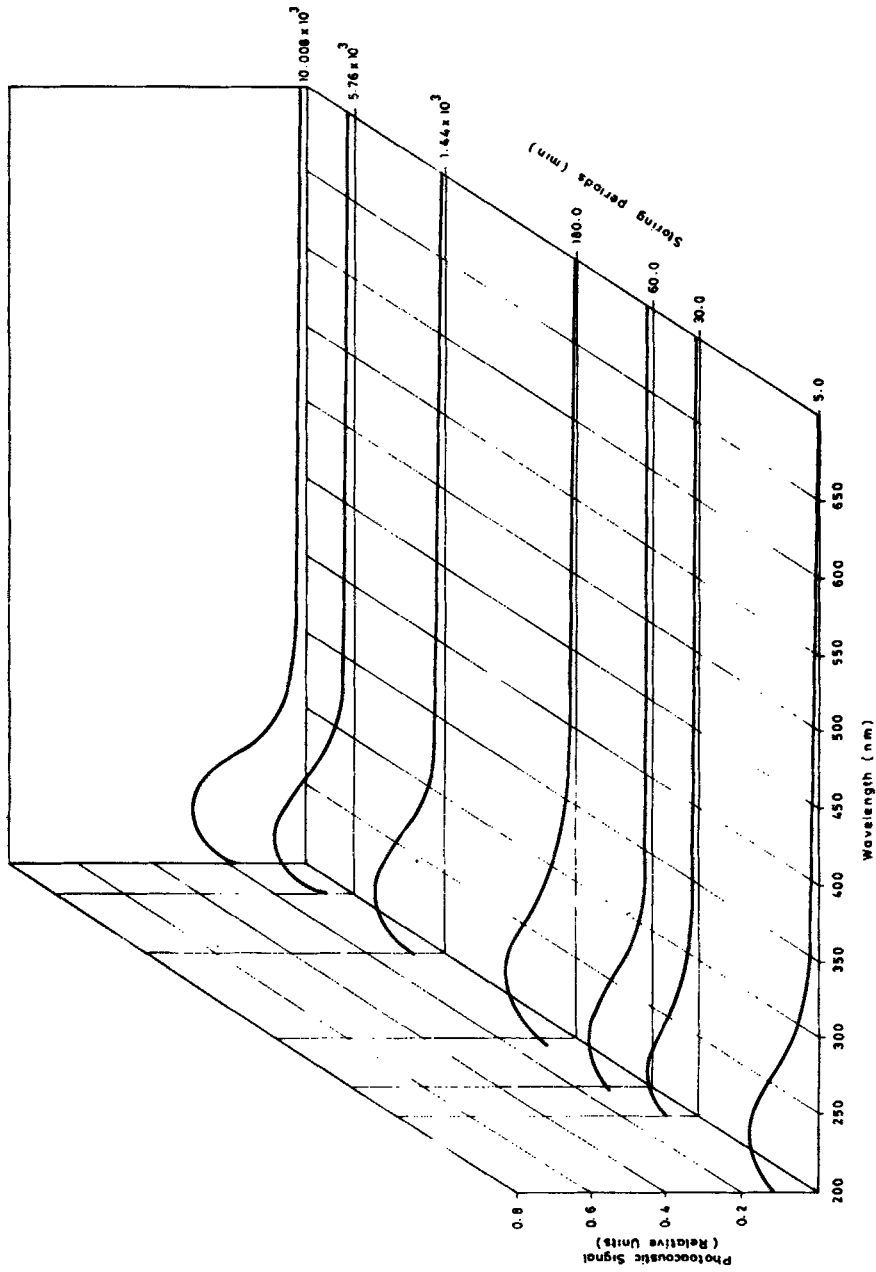


Fig. 5. PAS spectra of the rigid foam polyurethane sample previously heated at 165°C for 15 min and stored for 3 days. The sample was then exposed to UV irradiation for 3 min and stored for the periods indicated on the figure.

a minute amount as evidenced from Figure 2. This minute amount completely reacts with the traces of MBPI to form diphenyl urea.

If diamines existed in the sample in a large amount before its UV irradiation, the residues of the diamines that did not react with MBPI will show its characteristic PAS spectra in Figure 5. Since no traces of this band appear even if the sample was irradiated for less than 1 min with UV only, we concluded that these residues exist in the sample in very small quantities that cannot be detected using PAS.

In conclusion, catalyst residues play an important role in polyurethane degradation. As evidenced from the data presented in this work, catalyst residues are one of the major source for polyurethane degradation for temperatures $< 165^{\circ}\text{C}$. If, however, these residues are completely used in re-polymerization process of polyurethane, the resulting polyurethane was found to resist both UV and thermal degradation. This observation is of great industrial value.

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