

Thermal Degradation of Polyurethanes. Model Compounds

A. ORZESZKO and A. KOLBRECKI, *The Higher School of Fire-Fighting Officers, Warsaw, Słowackiego 52, Poland*

Synopsis

An analysis was carried out of degradation products of model compounds polyethylene glycol and ethylene diphenylcarbamate. Pyrolysis has been effected at 350 and 400°C under nitrogen and *in vacuo*. The products were analyzed by gas chromatography. Aniline, CO₂, CO, C₂H₄, CH₃CHO, etc., were found.

INTRODUCTION

Polyurethane resins provide valuable insulating material more and more frequently applied in the building trade and in many branches of industry. That is why investigations are being carried out to determine their thermal properties as well as the content and toxicity of gases emerging on pyrolysis and burning of the resins. Since only few references dealing with subject are known in the art, we have undertaken to study the course of thermal degradation of polyurethanes.¹⁻⁶ In order to avoid difficulties connected with the complex structure of polyurethanes, preliminary investigations have been carried out on the following model compounds: ethylene diphenylcarbamate (model I) representing the urethane group, and polyethylene glycol (model II) representing the aliphatic component of urethane resins.

EXPERIMENTAL

Ethylene diphenylcarbamate was prepared by reacting dried ethylene glycol with phenyl isocyanate at 80°C. The crude product was crystallized from benzene (mp 155°C). Loba-Chemie commercial-grade polyethylene glycol (mass number of 3600-4000) was employed without additional purification.

DTA tests were performed under nitrogen at a heating rate of 10°C/min.

Glass ampoules sealed under 1-2 torr were used in the pyrolysis process for quantitative determination of decomposition products. After the process, the ampoules were cut and their contents diluted with dioxane or acetone. For evaluation of pyrolysis gases, an ampoule crusher was employed, enabling direct introduction of the gases into the chromatographic column. Pyrolysis temperatures were determined from TG and DTA curves, 400°C for polyethylene glycol and 350°C for ethylene diphenylcarbamate. Pyrolysis time was 30 min. Gas-chromatographic analysis was carried out with nitrogen as carrier gas and

with a katharometer. A 2-m-long column filled with active charcoal was used for the determination of gaseous components.

Liquid products were determined on a column filled with Chromosorb W with OV-1 or fractonitrile phases.

The thermal degradation and chromatographic methods used in the study were based on the experience gained during cooperation with J. Żurakowska-Orszągh and co-workers at Warsaw University.⁷⁻⁹

RESULTS AND DISCUSSION

The TG and DTA curves shown in Figure 1 were obtained for model carbamate and polyethylene glycol. In both cases the degradation process is preceded by a melting point marked as endothermic effect. Degradation of carbamate starts quite rapidly at 230–240°C and quickly goes to 100% loss in weight, which occurs at 340°C. Polyol gradually loses weight at 200–240°C, and at 390°C it decomposes totally. Based on these findings, we fixed 30 min as pyrolysis time and 350 and 400°C as temperatures for models I and II, respectively. The compositions of the gaseous and liquid products of pyrolysis of carbamate (in mole % of products) were as follows: H₂, 0.4; CO, 1.8; CO₂, 49.6; C₆H₅NH₂, 48.1; CH₄, C₂H₄, C₂H₆, traces (see Fig. 2).

The results above make it clear that no HCN is produced under the given conditions of pyrolysis. Roughly, all carbamate nitrogen (91%) is converted to aniline and all oxygen (94%) converted to CO₂.

The presence of hydrogen cyanide observed by some researchers in pyrolytic gases emerging during oxidative decomposition of polyurethanes is likely to result from secondary decomposition of diamines produced in the process. The long time of release of HCN from polyurethane during oxidative decomposition seems to be one of the proofs supporting such interpretation.

Some reports present another mechanism of polyurethane decomposition comprising primary dissociation of urethane bond with recreation of substrate isocyanate and glycol.^{1,2,5,10} However, no traces of phenyl isocyanate or ethylene glycol have been found in the products of model compound pyrolysis. Pyrolysis

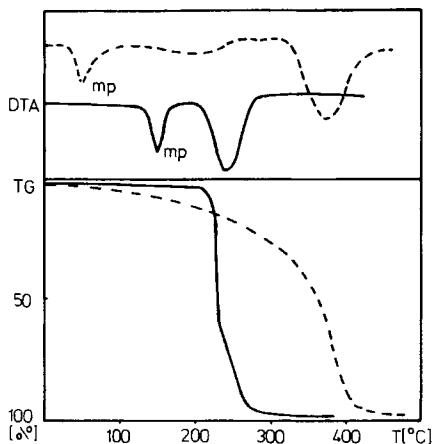


Fig. 1. TG and DTA lines of models I and II: (—) model I; (---) model II.

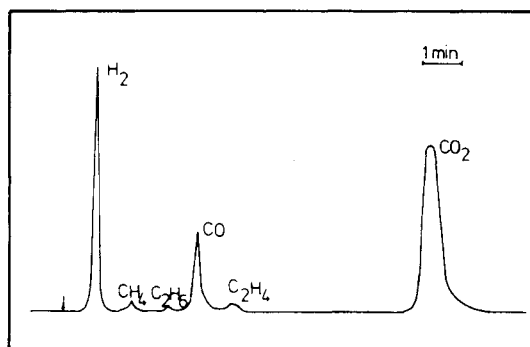
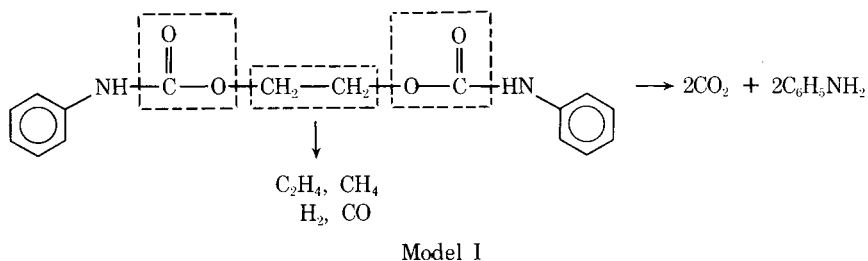


Fig. 2. Chromatogram of gaseous products of thermal degradation (model I, 2-m-long column with active charcoal, 80°C).

effected at lower temperatures (230–300°C) has not confirmed the production of these compounds either.

The reaction of isocyanate and alcohol is a typical addition reaction, i.e., an irreversible reaction. The presence of isocyanates in pyrolysis products claimed in some reports is likely to originate only in decomposition of other bonds of complex polyurethane structure, e.g., allophanate bond, biuret bond, and the like.³

Based on the above considerations and the results obtained in the experiments, it seems that the main process during pyrolysis of urethane compounds is equimolar production of aniline (91% N₂ in model I) and CO₂ (94% O₂ in model I). They result from decarboxylation of carbamate illustrated in following reaction scheme:



Moreover, a piecemeal dehydrogenation of aliphatic moiety goes along with the above reaction. The compositions of the thermal degradation products of polyethylene glycol (in mole % of products) were as follows: H₂, 2.0; CO, 20.6; C₂H₄, 49.6; CH₄, 2.1; CH₃CHO, 5.1; C₂H₅CHO, 1.3; C₂H₅OC₂H₅, 1.6; H₂O, 17.6 (see Figs. 3 and 4).

The composition of the pyrolysis products makes it clear that the decomposition process is more complex in this case. The number of components indicates that degradation of the polyglycol molecule proceeds statistically according to many schemes. The main reaction leads to production of ethylene (49.6%) and CO (20.6%). In addition, acetaldehyde and propionic aldehyde as well as ethyl ether are produced. These reactions are accompanied by dehydrogenation and

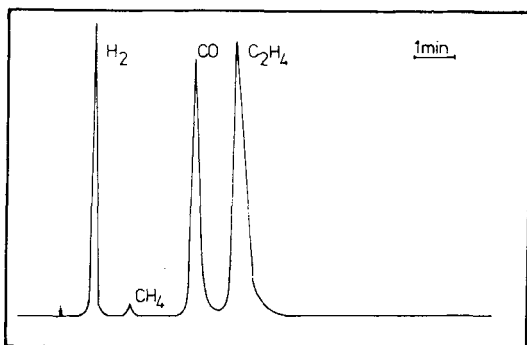


Fig. 3. Chromatogram of gaseous products of thermal degradation (model II, 2-m-long column with active charcoal, 80°C).

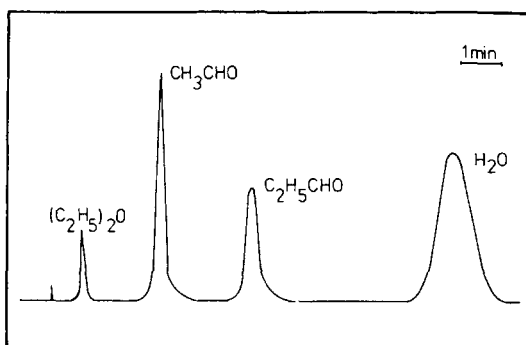
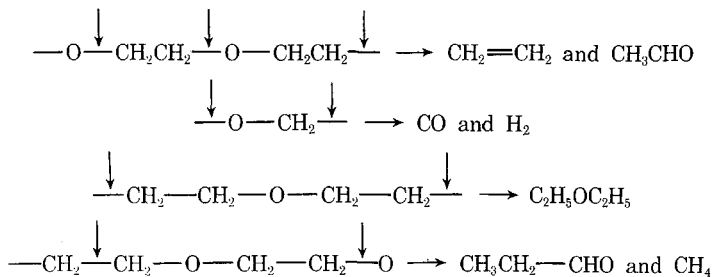


Fig. 4. Chromatogram of liquid products of thermal degradation (model II, 2-m-long column with Chromosorb W and 5% fractionitrile, 70°C).

dehydration as well as by processes producing traces of ethane and methane. The multidirectionality of degradation is likely to result from closeness of values of C—C and C—O bond energies in this compound. The scheme below shows the main mechanisms of polyethylene glycol pyrolysis:



Model II

CONCLUSIONS

(1) Owing to the application of the simple model compound monomeric carbamate, a single-direction nature of urethane bond degradation resulting in production of CO₂ and aniline has been revealed. This finding as well as lack of HCN in the products of thermal degradation may indicate that HCN produced during oxidative degradation results from secondary degradation of corresponding diamines. The absence of phenyl isocyanate and glycol in the products seems to confirm the impossibility of dissociation of the urethane bond to the starting materials.

(2) Polyethylene glycol degradation revealed multidirectionality of this process. Pyrolysis of the above model compounds enabled to identify sites in the polyurethane structure liable for formation of some toxic compounds, particularly HCN, CO, CO₂, and aldehydes.

References

1. F. D. Hileman, K. J. Voorhees, and I. N. Einhorn, in *Physiological and Toxicological Aspects of Combustion Products*, International Symposium, March 1974, Salt Lake City, NAS, Washington, D.C., 1976, p. 226.
2. D. W. Skidmore and P. R. Sewell, *Eur. Polym. J.*, **11**, 139 (1975).
3. G. W. Ball, L. S. Ball, M. G. Walker, and W. J. Wilson, *Plast. Polym.*, 290 (Oct. 1972).
4. H. H. G. Jellinek and K. Takada, *J. Polym. Sci. Polym. Chem. Ed.*, **13**, 2709 (1975).
5. E. Dyer and G. Wright, *J. Am. Chem. Soc.*, **81**, 2138 (1959).
6. T. Morimoto, K. Takeyama, and F. Konishi, *J. Appl. Polym. Sci.*, **20**, 1967 (1976).
7. J. Żurakowska-Orszàgh and S. Kobiela, *Polimery*, **21**, 348 (1976).
8. J. Żurakowska-Orszàgh and T. Chreptowicz, *Polimery*, **22**, 196 (1977).
9. J. Żurakowska-Orszàgh, A. Orzeszko, and S. Kobiela, *Eur. Polym. J.*, **13**, 787 (1977).
10. T. Mukaiyama and Y. Hoshino, *J. Am. Chem. Soc.*, **78**, 1946 (1956).

Received March 14, 1980

Accepted May 28, 1980