

The Analysis of Polyurethane Foams

II. Chemical Constitution of the Polymer*

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Synopsis

Efforts have been made to establish the chemical constitution of water-blown polyurethane foams. Specific reagents have been used to indicate the presence of biuret or allophanate linkages. Partial hydrolysis techniques have been used to degrade foams selectively and hence isolate parts of the chain network. These methods yield information which is not satisfactorily obtained from the examination of undegraded polymer and which is not available after total degradation. It has been shown that polyurea-type linkages are present in the chain network of both polyester and polyether foams.

INTRODUCTION

The total hydrolysis of a polyurethane foam produces information which is restricted to the identification of the constituent parts¹ and destroys any evidence of the ways in which these are combined in the original foam. Although the reactions of isocyanates with alcohols, water, and amines are superficially well known, the complexity of foam formulations and the fine balance of catalyst required as well as the simultaneous and consecutive reactions involved all suggest that the final product is likely to be very complicated. It was thought that partial hydrolysis methods would yield fragments of the polymer network of the original foam and that these would be more amenable to examination by a variety of chemical and instrumental methods.

DIRECT INFRARED EXAMINATION OF FOAMS

The infrared spectroscopic examination of flexible foams is best carried out by an attenuated total reflectance (ATR) technique.² The simple single-reflectance type of apparatus is usually sufficient, and sample preparation is reduced to a minimum as a regularly shaped piece of foam is readily mounted by pressing against the back of the ATR prism. Polyester urethanes absorb strongly at 5.8μ and in the $8-9 \mu$ region. For polyether urethanes the major absorptions are in the $9.0-9.6 \mu$ region, and the 5.8μ is of much weaker intensity. The other usual diagnostic features are the NH absorption and the amide II absorption at 6.5μ , together with

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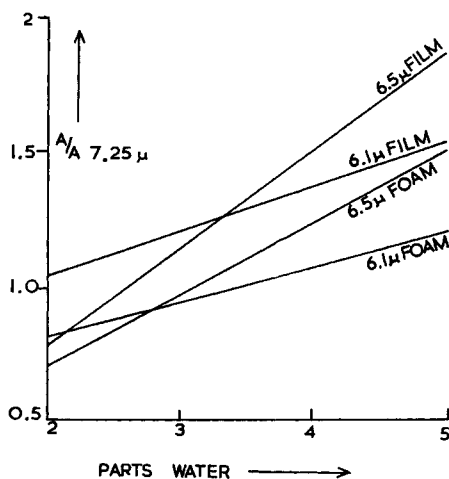


Fig. 1. The variation of infrared spectroscopic parameters with the amount of water in the formulation for foams and films (i.e., "collapsed foams") of PPG/TDI water-blown materials made at an index of 105. Plots shown are for 6.1 μ and 6.5 μ absorptions for 11 different foams and four film samples. In comparison, foam data for the 5.8 μ and 8.2 μ absorptions are reasonably constant, at average values of 0.48 (range 0.43 to 0.59) and 1.12 (range 0.98 to 1.21), respectively.

an absorption at 8.2 μ thought to arise mainly from the urethane linkage. Aromatic absorptions may be seen at 6.25 μ and after 12 μ . Urea groupings are indicated by the presence of an absorption at 6.1 μ , which results from the use of amine or water as a chain extender. Water-blown polyurethane foams usually have a 6.1 μ absorption of intensity approaching that of the 6.5 μ peak but greater than that of the 6.25 μ peak. Although rarely present, free isocyanate and carbodiimide give absorptions at 4.4 μ and 4.7 μ , respectively.

Although infrared spectroscopic measurements by ATR are not quantitative in the normal sense, calculated comparisons have been made between a number of polypropylene glycol (PPG) water-blown foams at the same toluene diisocyanate (TDI) index of 105 and from the same constituents, by referring each absorption to a common "thickness" peak. For example, the 6.1 μ and 6.5 μ absorptions measured in this manner have been plotted against the number of parts of water in the foam formulation and give apparently linear plots. A similar plot has been drawn for "collapsed foams," that is films made from similar foam formulations but replacing the foam-assister by a defoaming silicone and brushing out the mixture into a thin sheet from which the gas bubbles may easily escape. The plots obtained from genuine foams and "collapsed foams" are reasonably similar. (See Fig. 1.)

The plots of carbonyl (5.8 μ) and urethane (8.2 μ) absorptions tend to be independent of water content, but that of the aromatic peak (6.25 μ) depends on the amount of water in the formulation since the TDI content is adjusted to match the water content. Although these trends may be dis-

cerned easily, the general scatter of the results does not encourage a more quantitative treatment.

Allophanate and biuret groups have their carbonyl absorption very close to that of the urethane group and hence these are not readily distinguished from one another.

APPLICATION OF NMR SPECTROSCOPY TO THE ANALYSIS OF POLYURETHANE FOAMS

In our experience polyurethane foams are invariably insoluble unless some chemical bonds are broken. One convenient way of doing this is by refluxing in formic acid, when most polyurethane foams will dissolve after a few hours. Formic acid may be used as solvent for the nuclear magnetic resonance examination of aliphatic species but the solvent resonances almost obscure the aromatic signals. In this way poly(propylene glycol) may be distinguished very easily from poly(1,4-oxybutyleneglycol) and these two from polyesters.³ The diol part of polyesters may be identified, even when more than one diol is present, by making use of the three main aspects of NMR information—chemical shift values, splitting patterns,

TABLE I
NMR Data for Formic Acid Solutions

Material	Chemical shift, ^b τ	
Polyethers		
poly(propylene glycol)	6.3 (s)	8.7 (d)
poly(1,4-oxybutylene glycol)	6.3	8.3
Adipates		
ethylene	5.5 (s)	
diethylene	5.6	6.1
propane (1,2)	4.7, 5.5	8.6 (d)
butane (1,4)	5.7	8.25
hexane (1,6)	5.75	8.45
neopentyl	6.0 (s)	9.0 (s)
TMCB ^a	5.4, 5.5 (s)	8.8 (3s)

^a 2,2,4,4-Tetramethyl-1,3-cyclobutane diol.

^b s = Singlet; d = doublet; otherwise multiplets.

and integrated signal intensities. Formic acid as an NMR solvent shows a satellite peak at 3.5 τ and an acetic acid impurity at about 8 τ . The former we have used as a reference peak since tetramethyl silane (TMS) tends to separate, but the latter may be confused with the signals from methyl groups attached to aromatic nuclei. The information in Table I has been compiled from examples of polyurethane foams and elastomers.

Special foams made from polymeric diols have been found soluble in dimethyl acetamide-butylamine mixture, but the solutions appear to contain microgel. Consequently these have given only poor NMR spectra and no useful information on the types of linkages⁴ has been obtained so far.

PARTIAL HYDROLYSIS OF WATER-BLOWN POLYURETHANE FOAMS

Attempts have been made to find reagent mixtures which will cause partial breakdown of the foam and leave a residue which may then be examined by various other methods. A suitable rate of breakdown of polyester foam is achieved by refluxing a sample in a mixture of methanol (25 volumes) and concentrated hydrochloric acid (1 volume) for times up to 3 hr. The initial rate of weight loss is very large, but becomes very small after the first hour. In the earlier stages only the polyester parts are being attacked as no loss of nitrogen is experienced. Nitrogen is lost as breakdown proceeds, until a hydrolysis-resistant residue is left. In this type of treatment, a number of different polyester foams lose 75%–80% of their original weight and the residues contain about 70% of the original nitrogen. Changing the methanol/acid ratio from 100/1 to 10/1 does not cause much change in these results. Results are shown in Table II.

TABLE II
Partial Hydrolysis of Water-Blown Foams, in Acid^a

Sample	Index	Water	Refluxing time	Wt loss, %	Residue	
					N, %	N retained, %
PPG 1	105	4.55	8 hr	5		
Polyester 2	90	3.5	1 min	13	4.99	90.0
			3 min	29	5.78	84.9
			5 min	48	7.34	79.4
			10 min	66	10.75	74.6
			15 min	71		
			20 min	70		
			30 min	76	13.23	67.7
			1 hr	78		
			1½ hr	79		
			2 hr	79	15.18	66.6
Polyester diol	105	3.5	3 hr	79	15.18	66.5
			5 min	48	7.72	78.3
			10 min	66		
			15 min	50		
			30 min	74		
			1 hr	73		
			2 hr	73		
3 hr	75	14.56	71.3			

^a Reagent: methanol/hydrochloric acid 25:1.

The residue is found to be soluble in either dimethyl acetamide (DMA) or dimethyl sulphoxide (DMSO) but insoluble in pyridine, cold formic acid, and tetrahydrofuran. It has a urea-type infrared spectrum, and from its nitrogen content (values of about 15%) it is concluded that the residue is a polyurea, presumably a reaction product of TDI and water. A high molec-

ular weight polyurea of this type should have a nitrogen content of 18.9%, which would be reduced by the inclusion of polyester components.

These residues can be dissolved after refluxing for a few hours in formic acid, and NMR spectra of these solutions show the presence of diethylene glycol from the polyester but absence of adipic acid. From the ratio of diethylene glycol to TDI, as measured from the integrated NMR spectrum, and assuming a linear polyurea with a urethane-linked diethylene glycol unit at each end, it was calculated that the molecular weight of such an entity is about 1800. From the same sample a value of about 1200 was obtained from the nitrogen content assuming the same model. These values correspond to 6–10 TDI units in the polyurea segment. The residues gave an amorphous x-ray diffraction pattern with only an insignificant indication of crystallinity. After casting a film from DMA solution, the x-ray diffraction pattern was very similar, although a small increase in crystallinity was seen corresponding to a repeat distance of 4.3 Å.

For polyether foams it was found necessary to use methanolic potassium hydroxide under reflux for a few days to obtain a comparable breakdown. A rapid weight loss is experienced over the first few hours, but thereafter it

TABLE III
Partial Hydrolysis of Water-Blown Foams, in Alkali^a

Sample	Index	Water	Refluxing time	Wt loss, %	Residue	
					N, %	N retained, %
PPG 1	105	4.55	5 min	22	5.97	83.5
			10 min	30	6.29	78.6
			15 min	33	6.48	77.2
			30 min	41	—	—
			3 hr	64	9.81	64.6
			6 hr	73	12.84	62.6
			9 hr	70	—	—
			12 hr	71	13.10	67.6
			16 hr	78	—	—
PPG 1A	80	4.55	10 min	43	5.05	61.3
			40 hr	86	15.10	44.7
PPG 1B	120	4.55	10 min	32	6.29	67.8
			40 hr	82	15.76	44.8
PPG 2	105	2.7	9 hr	81	—	—
			12 hr	85	—	—
			18 hr	88	14.93	46.4
PPG 3	105	4.50	10 min	31	5.29	72.6
			40 hr	82	14.09	49.8
PPG Diol	105	3.5	40 hr	78	13.15	60.8
Polyester 1	90	3.5	cold	78	15.77	68.6
Polyester 2	90	3.5	cold	77	15.7	75

^a Reagent: 32 g potassium hydroxide, 32 ml water, made up to 500 ml in methanol.

becomes slower as a hydrolysis-resistant residue remains. This residue has a polyurea character similar to that produced from polyester foam, although it is difficult to remove every PPG chain from the polyurea block. Generally, the percentage weight loss figures vary between 80% and 90% and show some dependence on the formulation. The amount of nitrogen retained in the residue is in the 40%-50% range. Results are shown in Table III. These polyether foams were made with PPG triol having all secondary hydroxyl endgroups. As the hydrolysis must affect the urethane groups principally, since only trace amounts of PPG are present in the final residue, there is no direct way of counting the ends of the polyurea blocks obtained from polyether foams. The molecular weight of these urea blocks cannot be calculated from nitrogen determinations, although the latter figures support the proposed structure.

Difficulties have been experienced in analyzing the soluble portions of the hydrolyzates, but PPG, toluene diamine, and low molecular weight polyurethanes have been detected. Residues obtained after short times of hydrolysis are soluble in cold formic acid or DMA, although the infrared spectra are virtually unchanged from those of the original foams. Foams specially made from polyester and polyether diols have shown behavior similar to that described above.

AMINE TREATMENT OF FOAMS

The reagent system DMA/butylamine has been described⁴ as a specific reagent for decomposing allophanate and biuret groupings in polyurethanes, which enables some elastomeric polyurethanes to be made soluble. Polyether foams do not dissolve in this reagent, as the triol backbone still forms the basis of a three-dimensional network. However, swelling measurements after two days in DMA containing 5% or 15% butylamine were greater than those made in DMA alone, indicating that some chemical attack had taken place⁵ and some crosslinks broken. These measurements, expressed as the ratio of the swelling in the presence of amine to the swelling in DMA only, give results in the range 1.3 to 1.9 for foams of TDI index 105. The ratio appears to be independent of the water content in the foam formulation. Results in the range 1.0 to 1.1 have been obtained for foams of 80 and 95 index, while one foam of 120 index was found to dissolve in the presence of amine.

Polyester foams dissolve in *n*-butylamine if the amine concentration is above about 5%, thus making swelling measurements unreliable. The amines (when used as 50% solution in DMA) that have been found to dissolve polyester foams are *n*-butylamine, piperidine, and benzylamine, but those that are ineffective include *tert*-butylamine, diethylamine, diisobutylamine, and dibenzylamine.

This behavior yields qualitative evidence that biuret or allophanate groups exist in foams as integral parts of the three-dimensional network. In polyester foams, the network may be completely solubilized when these

groupings are destroyed, but in comparison the effect on polyether foams is less significant. This difference could arise from the fact that polyether foams are made from trifunctional polyol, whereas the functionality of the polyester material is about 2.5. In support of this, a foam made from a polyether diol was found to be soluble in a mixture of 5% butylamine in DMA.

CONCLUSIONS

These observations suggest the following:

(1) The structural units constituting the linkages in polyurethane foams appear to be generally similar for polyether and polyester foams, although there may be detail differences between the two types. Polyurea-type block segments have been isolated from both types of foam and the lengths of these blocks have been indicated for polyester foams.

(2) Amine treatment shows that allophanate and/or biuret groupings are present in both types of foam.

(3) Diethylene glycol terminal units found attached to the hydrolysis-resistant polyurea blocks may be taken as an indication that these blocks are chemically combined into the polymer network.

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