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Color Formation in Polyurethanes*

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INTRODUCTION

In the past few years there has been a tremendous growth in the chemistry of polyurethanes. This includes a large number of types and many different synthetic approaches, but very little has been published or apparently is known about the problem of color development.

Previous experimental work has been directed towards the isolation of degradation products of polyurethanes under heat,[1,2] ultraviolet radiation, and more highly energetic radiations.[3] The explanations for color formation were not satisfactory. It was believed that the yellowing of polyurethanes was due to oxidation of free amino groups which is strongly catalyzed by light.[4]

In general, there are two ways open to stabilize polymers: either to add an antioxidant or ultraviolet screening agent[5,6] or secondly to develop an inherently more stable polymer by suitable chemical modification. Applications of this latter approach to polyurethanes are the use of a diisocyanate in which the isocyanate group is separated from the aromatic ring by an alkylene group which prevents resonance within the molecule[4] or the treatment of polyurethanes with monoisocyanate, ketene, formaldehyde, acetic anhydride, or ethylene oxide in gas phase or in solution.[7] Particularly aliphatic, aromatic, or aryl-aliphatic monoisocyanates are quite effective. It has been found that protection is enhanced with an increase in the period of treatment of polyurethane foams with monoisocyanates, but the reason of this stability has not been clearly defined.

The present work was undertaken to clarify the mechanism of thermal degradation and also to discover another way of stabilizing the polyurethane synthesized from ethylene glycol and tolylene 2,4-diisocyanate. The degradation of the polymer was studied by infrared and ultraviolet spectra of films cast on rock salt plates, and isolation of the degradation products. The rate of color formation was measured by the color index of pyrolyzed film as defined in a previous work.[8]

EXPERIMENTAL

Apparatus Used

Infrared spectra were obtained on a Baird infrared spectrophotometer, Model B. Ultraviolet spectra were taken on a Perkin-Elmer Spectracord,

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Model 4000. For gas chromatography, a Perkin-Elmer vapor fractometer, Model 154, was used. Melting points were taken on a Fisher-Johns melting point apparatus with appropriate correction. Potentiometric titrations were carried on a Beckman pH meter, model G. For aging studies, an air oven from Precision Scientific Company was used; the temperature was maintained at 155 ± 2°C.

Reagent

Ethylene glycol (Matheson, Coleman and Bell, b.p. 195–197°C.) was shown to be chloride-free by potentiometric titration,[9] giving one single peak on gas chromatography[10] after one distillation under reduced pressure (67°C./6–7 mm.).

Tolylene 2,4-diisocyanate (TDI) (National Aniline Division) contains an extremely small quantity of the 2,6 isomer as shown by a shoulder at 12.7 μ in the infrared spectrum.[11] A spectroscopically pure sample was obtained by careful fractionation. Study of the color index and weight loss of the pure 2,4-polyurethane and an 80/20 mixture of 2,4- and 2,6-polyurethanes did not show much divergence at 150–155°C. Therefore, in further experiments in the identification of degradation products and the measurement of CO_2 evolved, TDI was simply purified by distillation under reduced pressure; the center cut was used.

Synthesis

Linear Polyurethanes. Polyurethane was prepared by condensing equimolar quantities of TDI and ethylene glycol in nitrogen in reagent-grade ethyl acetate as solvent at 60–65°C. for $2^1/_2$ days. The yield was 90–95%.

To study the catalytic effect of chlorine,[12,13] the following polymers were synthesized: polymer A containing 0.002 mole CH_2OHCH_2Cl per 0.1 mole of TDI (yield 95%); polymer B containing 0.006 mole CH_2OHCH_2Cl per 0.1 mole of TDI (yield 90%); polymer C containing 0.002 mole monocarbamoyl chloride of TDI per 0.1 mole CH_2OHCH_2OH (yield 80%); polymer D containing 0.004 mole monocarbamoyl chloride per 0.1 mole CH_2OH-CH_2OH (yield 78%). The carbamoyl chloride was obtained by bubbling dry HCl into a solution of TDI in benzene.

Crosslinked Allophanate Polyurethane. A typical preparation was as follows. In a dry 500-cc., three-necked flask equipped with stirrer, condenser, drying tube, and nitrogen inlet was dissolved 9.44 g. (0.04 mole structural unit) of polyurethane in 200 cc. pure, dry tetrahydrofuran (THF). To this solution was added 6.97 g. (0.04 mole) of tolylene diisocyanate and 3 mole-% triethylenediamine (Dabco). The solution was refluxed for 36 hr. The polymer precipitated from the solution. After filtration and washing with pure THF, the polymer was then dried in vacuum for 24 hrs. at 70°C. The yield was 90%.

ANAL. Calc. for $(C_{20}H_{18}N_4O_6)_n$: C, 58.53%; H, 4.39%; N, 13.65%. Found: C, 58.77, 58.57%; H, 4.86, 4.74%; C, 13.53, 13.63%.

Polycarbodiimide. This was prepared by heating 20 g. of TDI at 230–240°C. The extent of reaction was measured by the quantity of CO_2 evolved (76%). The residue was then washed with acetone and ether, ground, and dried. The infrared spectrum of the yellow powder showed a small band at 4.4 μ and a strong band at 4.7 μ, the latter characteristic of the N=C=N structure.[14]

Polypseudourea Ether. A slight excess of ethylene glycol (ratio of ethylene glycol:carbodiimide = 1.1) was allowed to react with the polycarbodiimide at 150–160°C. for 36 hr. in a nitrogen atmosphere. The compound obtained was washed with ether and dried.

The infrared spectrum showed a very small band of carbodiimide due to incomplete reaction resulting from a partial evaporation of ethylene glycol from the reaction mixture and other absorption peaks at 3, 3.4–3.5, 6.2, and 6.63 μ. Dyer and Newborn[1] reported in the degradation of bisurethane of methylene bis(4-phenyl isocyanate) and benzyl alcohol a pyrolysis residue absorbing at 3.0, 3.5, 6.2, and 6.65 μ.

ANAL. Calc. for $(C_{15}H_{16}N_4O_2)_n$: C, 67.08%; H, 5.59%; N, 17.09%. Found: C, 67.02%; H, 5.64%; N, 17.39%.

Aging Studies

Color Index of the Polymers. The color index I was defined as

$$I = \frac{\%\ \text{Transmittance at } \lambda_1}{\%\ \text{Transmittance at } \lambda_2} \times 1000 \qquad (9)$$

where $\lambda_1 < \lambda_2$.

In the first experiments, where very thin films were used, λ_1 and λ_2 were chosen to be 340 and 500 mμ, respectively. In later experiments, to obtain good control of film thickness and improve reproducibility of the results, thicker films were prepared, and spectra were taken in the visible region at 650–360 mμ; λ_1 and λ_2 were then 360 and 500 mμ, respectively.

Three rectangular rock salt plates of the same thickness were polished and cleaned to complete transparency. Each one had a central 1.6 × 1.5 cm. rectangular hole, 1 mm. in depth. The rock salt plates, mounted in the same way on cardboard, were set in the sample beam and reference beam of the spectrophotometer and matched by adjusting the set of knobs controlling the 100% line. Once the instrument had been set, care was taken to keep the instrument always in the same experimental conditions. The 100% line was checked regularly with two of the three plates having no films on them. Use of the band adjustment was necessary if the 100% line deviated.

Solutions of 0.5% and 2% of polyurethane were used for thin and thick films, respectively. The films were cast on rock salt and dried 1 hr. at room temperature and 2 hr. at 75–80°C. The films were then aged at 155°C. in an air oven. Precautions were taken to eliminate moisture by letting the films cool to room temperature in a desiccator before every run. Spectra were taken at regular intervals of time.

Infrared Studies. The same technique as described above for studies of the color index was applied. Films were cast from a solution of 2% of polyurethane in THF. As the change in the infrared pattern of aged films was quite slow, a differential technique was used to detect more easily minor changes during the thermooxidative degradation. An unaged polymer film was used as reference. An aged film of the same thickness was put in the sample beam and differential plots were obtained at given intervals of time. The initial plot was approximately a flat line. A decrease of an absorption peak in the aged film is shown by a peak upward, and a new absorption peak by a peak downward.

By careful control of various factors, for the differential as well as for the ordinary methods, it was possible to keep constant the position of the baseline of the spectrum on the chart.

Weight Loss Study. Thick films of approximately equal weight were cast on watch glasses from a solution of 5% of polymers in THF. These films were heated for 17 hr. at 65–70°C., then 8 hr. under reduced pressure at the same temperature in order to remove the solvent. Films were then aged at 155 ± 5°C. The weight was determined at regular intervals of time. The weight after 1 hr. of pyrolysis was taken as the baseline for weight to insure that all the solvent was completely removed.

Pyrolysis of Polyurethane Powder. The pyrolysis was carried out in a 100-cc. three-necked flask. A slow current of dry nitrogen, air, or oxygen swept at a rate of 20–22 cc./min. the whole apparatus, including the reaction flask equipped with condenser, thermometer, gas inlet and outlet, a trap cooled by a Dry Ice–acetone bath, a calcium chloride U-tube, a three-way stopcock, each end of which was connected to a U-shaped Ascarite tube. By turning the stopcock in a suitable direction, it was possible to measure without any loss the amount of CO_2 evolved as a function of time.

Pure and dry nitrogen was obtained by bubbling nitrogen (Linde, H.P. dry) into an alkaline solution of pyrogallol, then into sulfuric acid, then passing it through a tower of $CaCl_2$, a tower of Ascarite and a tower of molecular sieves. Dry air and oxygen were obtained by the same way with the pyrogallol solution removed. In one experiment of degradation of polyurethane allophanate, a trap cooled by a Dry Ice–acetone bath was inserted just before the reaction flask to remove any possible trace of moisture. In degradation of deuterated polyurethane allophanate synthesized from a deuterated glycol (CD_2OHCD_2OH), dry glass tubing was used to carry the gas.

Isolation of Products

Ethylene oxide was detected by bubbling the gas mixture from the reaction flask into a 40% KSCN solution in presence of phenolphthalein[15] or by infrared determination of the gas collected in a gas cell. Ethylene glycol and water were identified by their infrared spectra, and 2,4-toluenediamine by infrared and melting point determinations. The residue after degradation at 152°C. was extracted with THF in a Soxhlet extractor from which

the unreacted polyurethane was separated. Polyurea was separated by extraction of the remainder with hot DMF. Polypseudourea ether and some intermediate structures were insoluble in both these solvents.

RESULTS AND DISCUSSION

Color Index Measurements on Film Heated in Air at About 155°C.

Thin Films. Very thin films (21 μ) possessing initially approximately 50% transmittance at 283 mμ were obtained for different samples. During the degradation, the urethane peak became broader and less defined. As might be expected, the films showed a progressive increase in the absorption from about 320 to 400 mμ as the color progressed from a very light yellow to a medium yellow. No new defined peak was observed, however.

Comparative studies of the polyurethane films aged at 155 ± 2°C., although approximate due to the difficulty in working with too thin films, showed that the rate of color formation was only slightly different for pure 2,4-polyurethane and the 80/20 mixture of 2,4- and 2,6-polymer (Fig. 1). The latter was colored a little faster at the beginning. Polyurethanes containing monocarbamoyl chloride as impurity (polymers C and D) had about the same decrease in color index, clearly much larger than that of the pure 2,4- and mixed polyurethanes.

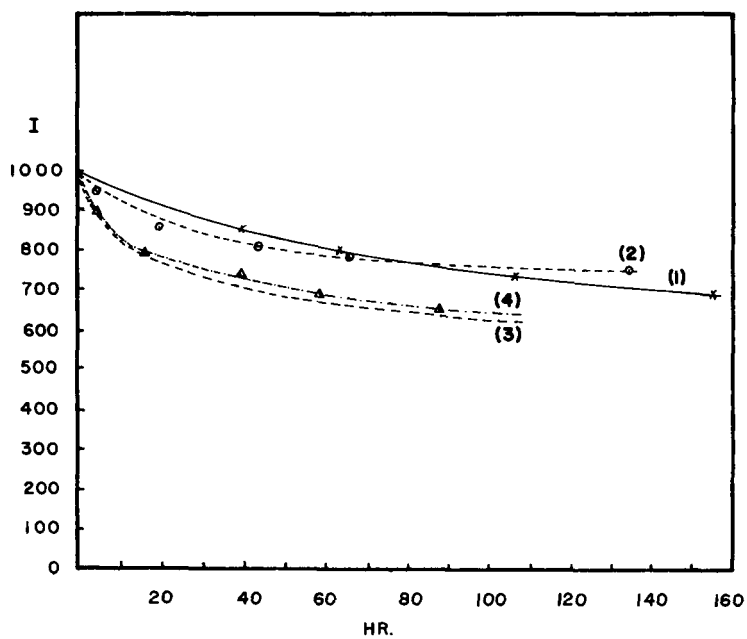


Fig. 1. Color index of polyurethanes *I*: % T at 340 mμ/% T at 500 mμ × 1000: (1) polyurethane from TDI and ethylene glycol; (2) mixture of polyurethanes; (3) polyurethane containing 2% monocarbamoyl chloride; (4) polyurethane containing 4% monocarbamoyl chloride.

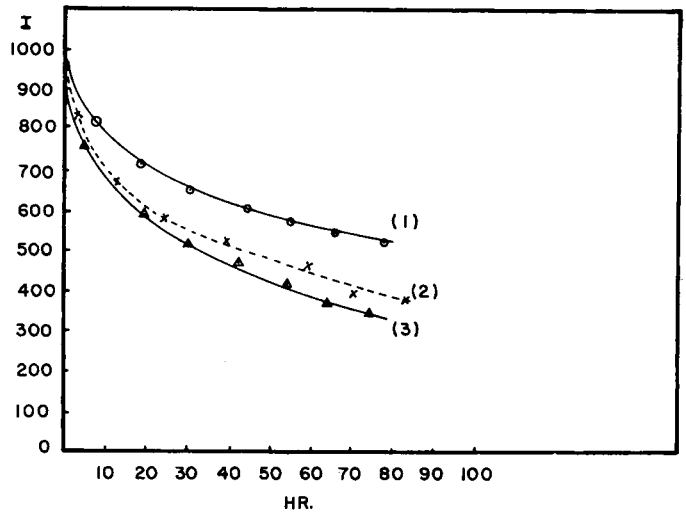


Fig. 2. Color index of polyurethanes *I*: % T at 360 mμ/% T at 500 mμ × 1000: (*1*) polyurethane from TDI and ethylene glycol; (*2*) polyurethane containing 4% monocarbamoyl chloride; (*3*) polyurethane containing 6% CH_2OHCH_2Cl.

Thicker Films. Polymers B and D appeared more colored than the pure 2,4-polyurethane during the thermal degradation (Fig. 2).

Infrared Studies of Films

The two methods of recording the infrared spectra, i.e., the differential and ordinary methods, gave only qualitative data. The main cause was that the degradation products contained a great amount of carbonyl functions and NH group absorbing almost at the same wavelengths; this made it impossible to follow quantitatively changes during pyrolysis. The only peak suitable for study of the decomposition of the urethanes was the 9.4 μ peak corresponding to the C—O—C deformation in the carbamate group. During the degradation the decrease of this peak was considerable, but it was not possible to identify the new products formed.

All the polyurethanes containing the NH of the carbamate group showed the same change in absorption bands in the infrared (Fig. 3).

Variation of Peak Absorption during Degradation in the Differential Method. Peaks which decreased were: the NH band at 3 μ, the CH_2, CH_3 band at 3.4 μ, the carbamate band at 5.9 μ, the band at 6.25–6.3 μ (NH ?), the absorption due to C = O deformation at 8.2 μ, the C—O—C deformation peak at 9.4 μ, and the band at 13 μ. Bands which increased during the pyrolysis were those at 5.7–5.75 μ, 6.0–6.08 μ, and 13.2 μ. The intensity of the band at 5.7–5.75 μ increased slowly at first, then leveled off around 40 hr., and subsequently decreased; in some cases this band did not appear. The significance of this band is not yet fully understood. The band at 6.0–6.08 μ is characteristic of the urea structure found in the degradation of

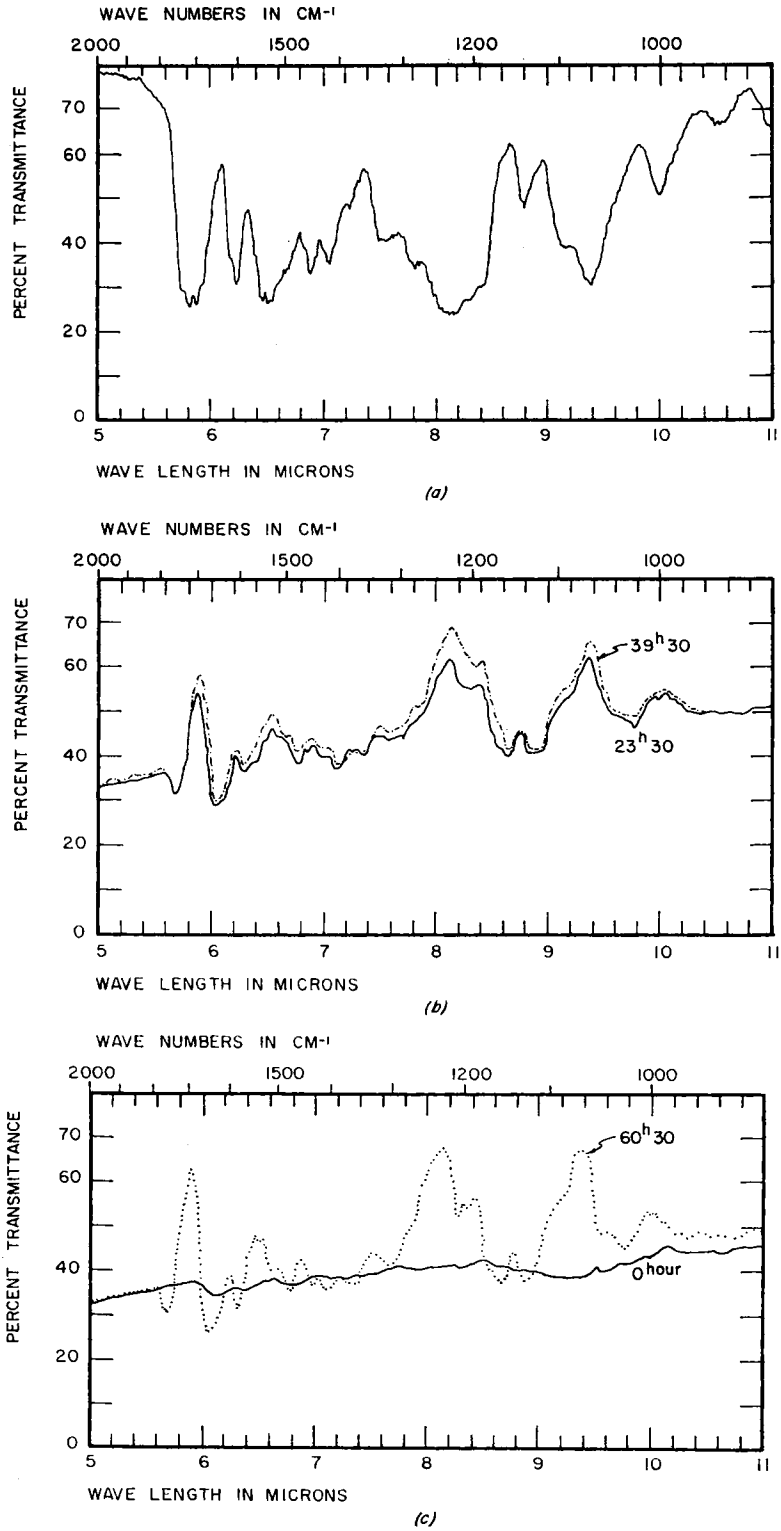


Fig. 3. (*a*) Infrared spectrum of unsubstituted polyurethane; (*b*) infrared spectra of degraded polyurethane at various instants (differential method); (*c*) infrared spectrum of degraded polyurethane after 60.5 hr. (differential method).

polyurethane powder. In the differential method, these bands were seen quite early. The slight increase in absorption at 13.2 μ was characteristic of the urea structure or the allophanate structure. During the pyrolysis the band at 13 μ shifted more and more towards 13.2 μ.

Variations in Absorption by the Ordinary Method during Degradation. About the same variations were observed but less clearly than in the differential method. The 5.7–5.75 μ peak was not seen in this case. The peak at 6.25 μ became broader; more resolution occurred in the region 6.5–6.7 μ. The shift of the 13 μ band to 13.2 μ was visible. The weak peak at 7.06–7.07 μ was split into two weak peaks at 7.05 and 7.10–7.12 μ.

Weight Loss

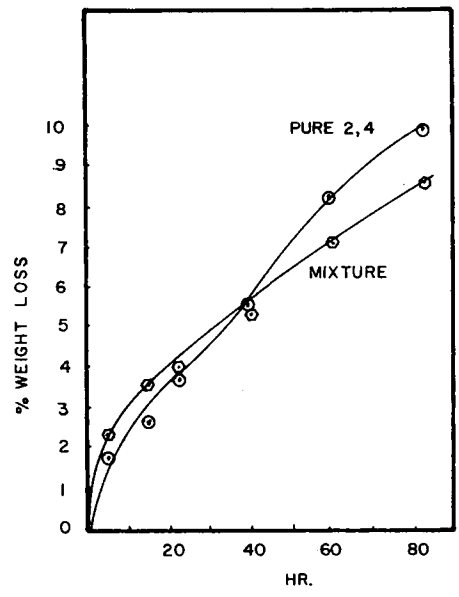
Pure 2,4- and Mixed Polyurethanes. The results are reported in Figure 4. The loss in weight of the 80/20 mixture of 2,4- and 2,6-polymers was slightly greater than that of the pure 2,4-polyurethane at the beginning, then became slightly smaller after 80 hr. The mixture appeared to be slightly more colored than the 2,4-polyurethane.

Polymers with Selected Impurities. The loss of polymers A and B was smallest. C had about the same loss as the pure polyurethane; loss of polymer D was slightly greater. It was interesting to note that after the first six hours of pyrolysis, polymers B and C had about the same color intensity, polymer A was light, while polymer D was quite colored. Polymers A, B, C, and D were all more colored than the pure 2,4-polyurethane in our experimental conditions, the plot in weight decrease at time t versus time for different samples did not show any clear relationship with the color index between the pure and chlorine-containing polymers (Fig. 4).

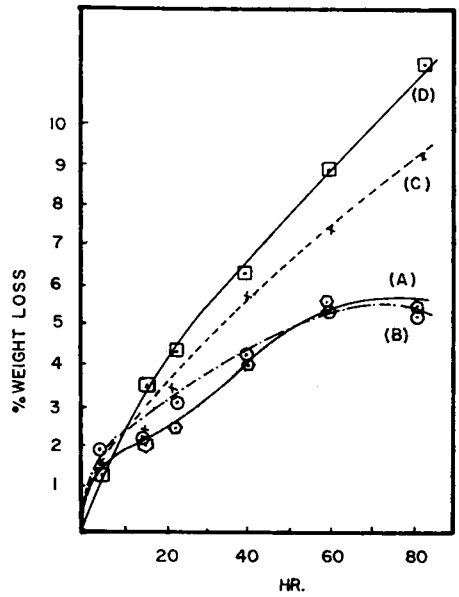
Pyrolysis of Polyurethane Powder

The study of the degradation of polymer films did not give a clear picture of the mechanism of degradation. In order to make assignments for the bands formed or disappearing in the infrared spectra of pyrolyzed films and also to propose a plausible mechanism of pyrolysis, it was obvious that identification of the products of degradation was necessary.

The degradation of polyurethane powder was therefore carried out at various temperatures up to 215°C. under CO_2-free, dry nitrogen, air, or oxygen. At 150–155°C. the evolution of carbon dioxide in nitrogen was quite slow, though after 20 hr. yellowing was already visible, and this increased with time. Presence of air or oxygen did not affect the rate of evolution of carbon dioxide appreciably during the first 70 hr., but later on it did increase considerably carbon dioxide formation (Figs. 5 and 6). Oxygen proved to be more effective than air. In air, the polyurethane powder turned slightly yellow after about 20 hr., and the color increased with time apparently slightly faster than in nitrogen, and later on increased considerably. The polymer in air or oxygen turned brown while in nitrogen, it was only yellow after about the same length of time. If the degradation was carried out at higher temperature, the polymer turned dark brown



(a)



(b)

Fig. 4. (*a*) Weight loss of polyurethanes at 155° ± 5°C., (*b*) weight loss of polymers at 155° ± 5°C.: (A) polyurethane containing 0.02*M* CH_2OHCH_2Cl per mole of TDI; (B) polyurethane containing 0.06*M* CH_2OHCH_2Cl per mole of TDI; (C) polyurethane containing 0.02*M* monocarbamoyl chloride per mole of ethylene glycol; (D) polyurethane contairing 0.04 *M* monocarbamoyl chloride per mole of ethylene glycol.

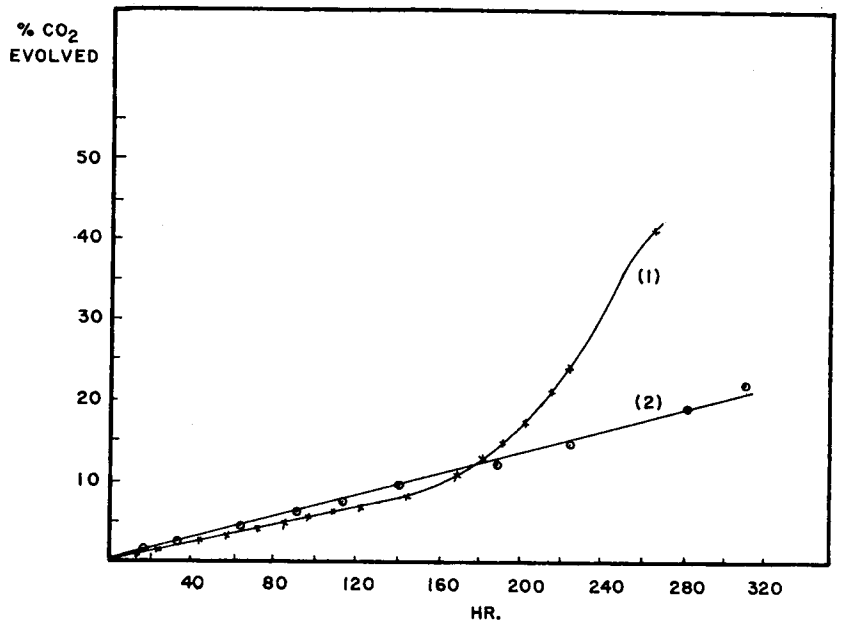


Fig. 5. Loss of CO_2 from the degradation of polyurethane powder: (1) degradation of polyurethane in N_2 (dotted line) then in air (full line); (2) degradation of linear polyurethane N_2.

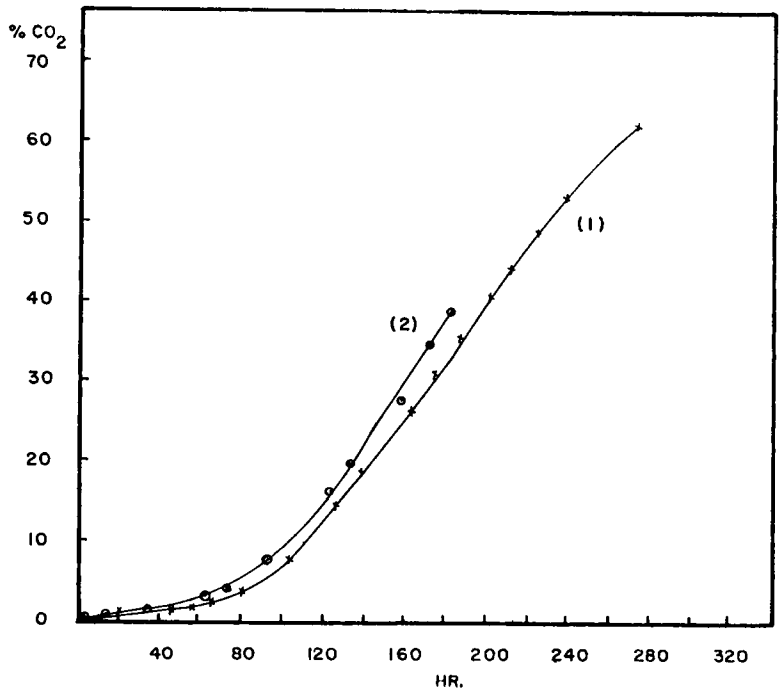


Fig. 6. Loss of CO_2 from the degradation of polyurethane powder: (1) degradation of polyurethane in air; (2) degradation of polyurethane in oxygen.

TABLE I
CO_2 Evolution on Pyrolysis of 2,4-Polyurethane in Nitrogen

	Expt. No.		
	1	2	3
Pyrolysis temperature, °C.	205 ± 10	209 ± 10	200 ± 10
Pyrolysis time, hr.	36	30	20
Amt. polyurethane, mg.	4000	4000	4000
Amt. solvent + water, mg.[a]	310	200.4	—
Amt. CO_2, mg.	1060.1	1211	1202.5
Amt. CO_2, mole	24	27	83
Amt. CO_2, %	73	83.5	83
Pyrolysis residue, mg.	1912	2139.2	2361.2
Amt. water, mg.[b]	95	12	—

[a] Recovered from trap.
[b] Increase in weight of $CaCl_2$.

TABLE II
Degradation Products from Pyrolysis of 2,4-Polyurethane

	Expt. No.				
	4	5	6	7	8
Carrier gas	N_2	N_2 + air	Air	O_2	N_2
Temperature, °C.	150–170	153 ± 2	153 ± 2	153 ± 2	152 ± 2
Time, hr.	69	265.5	352	184	310
Amt. polyurethane, mg.	5000[a]	4770	4740	4740	4720
Amt. solvent, mg.	[b]	230	282	260	280
Amt. products, mg.					
CO_2	1084 (60%)	740 (42%)	1266 (72%)	685 (39%)	414 (23.52%)
Ethylene glycol	[c]	[b]	108	60	—
Residue		4033	3338.8	3986	—
Unreacted polyurethane	[c]	1753	586	2035	—
Polyurea	[c]	800	490	1188	—
Intermediate structure	0	498	1201	298	—
Polypseudourea ether	[c]	0	821	0	—
Water[d]	21	220	189	130	—
2,4-Toluenediamine	[c]	0	0	0	—
Total recovery, %		104	104	102	

[a] Includes weight of solvent.
[b] Not determined.
[c] Identified qualitatively.
[d] Increase in weight of $CaCl_2$.

very rapidly, the rate of carbon dioxide evolution was quite fast, and thus masked the effect of oxygen.

Products of Degradation

In air or oxygen at 150–155 °C. or in nitrogen at 150–170 °C., the following products were obtained in general from pyrolysis of 2,4-polyurethane: unreacted polyurethane, carbon dioxide, water, ethylene glycol, ethylene

TABLE III
Pyrolysis of Crosslinked Allophanate Polyurethane at 152°C.

	Expt. No.						
	1 (TD1)	2 (TD1)	3 (TD1)	4 (TD1)	5 (MD1)	6	7
Pyrolysis medium	O_2	O_2	O_2	O_2	O_2	N_2	N_2
Pyrolysis time, hr.	217	174	194.5	296.5	294	122	296
Amt. polyurethane, mg.	8847	4100	4100	3911	4860	4100	3890
Amt. polyurethane, mmole	21.5	10	10	9.5	10	10	9.5
Amt. CO_2, mg.	1575	669	744	708	494.5	721.4	624.2
Amt. CO_2, mmole	35.8	15.2	16.92	16.09	11.23	16.4	14.2
Amt. CO_2, %	83	76	84.6	84.68	56.2	82	75
Amt. water, mg.	328[a]	410	450	357.5	420.8	43	79
Amt. water, mmole	18	22.8	25	20	23.4	2.3	4.4
Residue, mg.	7244	3438	3388	3378.2	4395	3354	3156.6
Total recovery, mg.	9147	4517	4582	4443.7	5310.3	4118	3859.8

[a] No trap cooled by Dry Ice was used, so a certain loss of water might be expected.

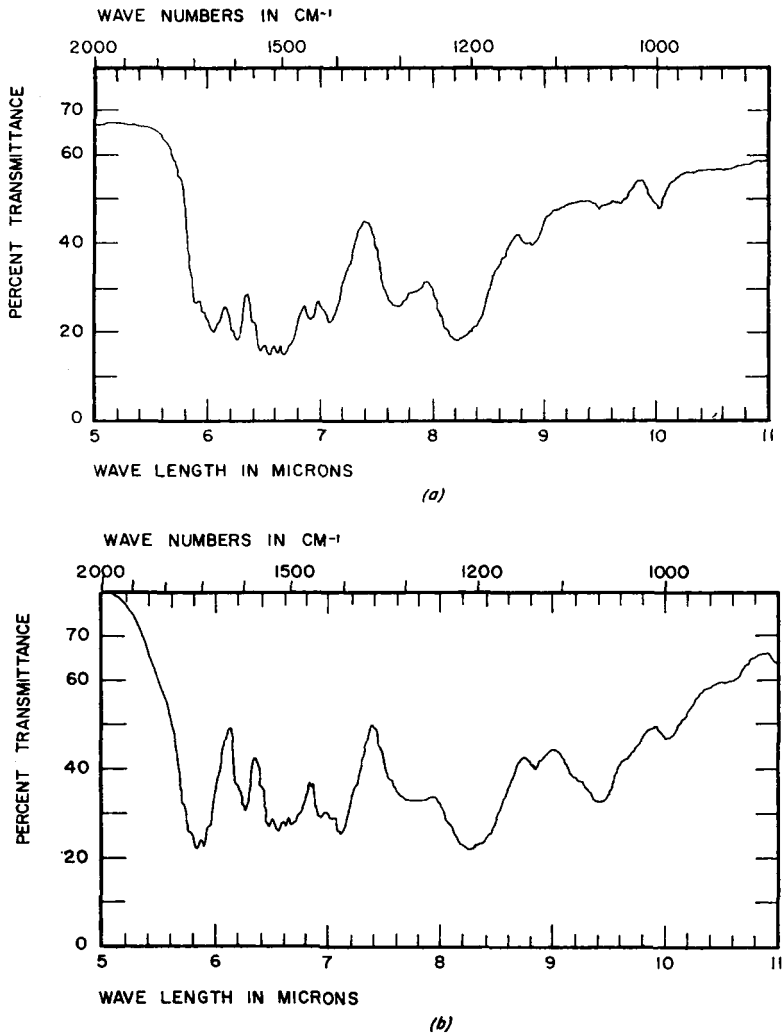


Fig. 7. (*a*) Infrared spectrum of the polyurea synthesized from TDI and 2,4-toluenediamine; (*b*) infrared spectrum of the polyurethane allophanate synthesized from polyurethane and TDI.

oxide, a polyurea, and polypseudourea ether. A few crystals of 2,4-toluenediamine were also collected during the pyrolysis in nitrogen at 150–170°C.

In nitrogen at 200–215°C., rate of carbon dioxide evolution was very fast; the products obtained were ethylene glycol, ethylene oxide, 2,4-toluenediamine, a small quantity of water, and a residue which was mainly polypseudourea ether. Loss of carbon dioxide was about 80% of the total amount of CO_2 (calculated on the assumption that 2 moles of CO_2 would evolve per structural unit). Table I and II summarize the experimental data found in the pyrolysis of polyurethanes.

Identification of the Polyurea Structure

The polyurea (A) obtained from degradation was compared to a polyurea (B) synthesized from reaction of equimolar quantities of TDI and 2,4-toluenediamine and to the residue (D) obtained by pyrolysis of the allophanate polyurethane (C) crosslinked with TDI. The infrared spectrum of the residue (D) was identical to that of the polyurea found in the

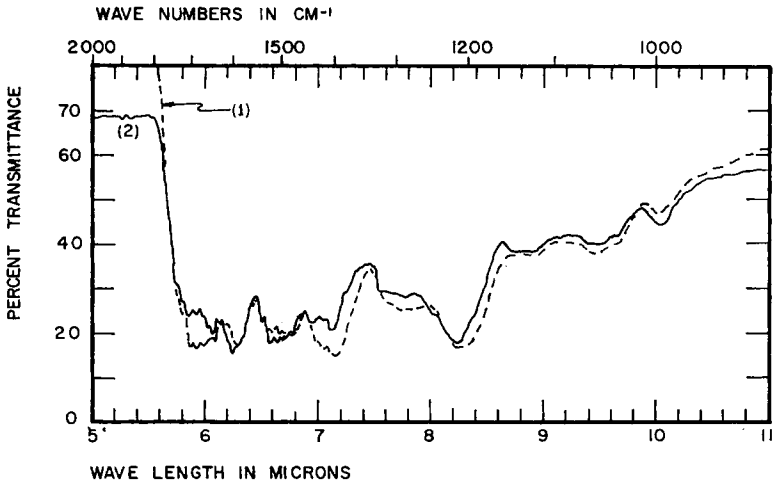


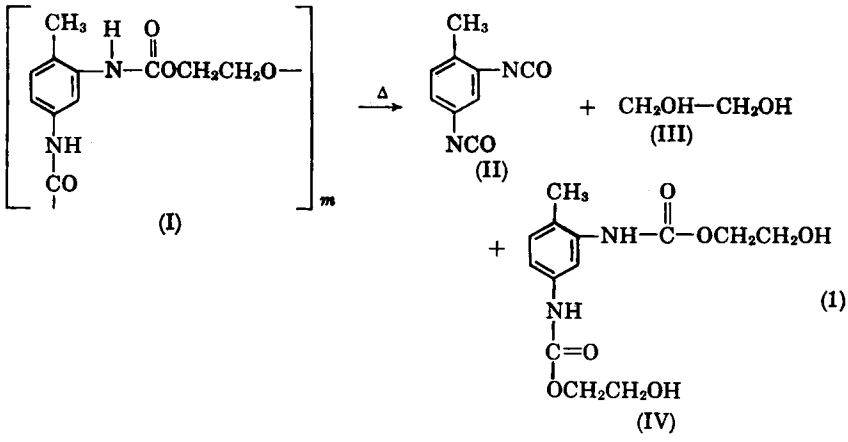
Fig. 8. (1) Infrared spectrum of polyurethane allophanate degraded in oxygen; (2) infrared spectrum of the product obtained in the degradation of polyurethane in air.

degradation of linear polyurethane with the exception of the band at 7.1 μ which was much sharper for the degraded crosslinked polyurethane. A comparison of the infrared spectra of these four materials (Figs. 7 and 8) indicates that the polyurea A formed in pyrolysis is a mixture of unreacted polyurethane, polyurea B, and residue D. The weak band at 7.1 μ was attributed to the presence of a small amount of residue D. The polypseudourea ether was identified by comparison with an authentic sample.

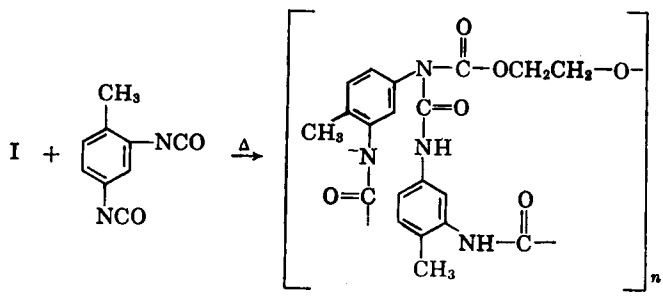
Proposed Mechanism

In nitrogen at 150–170°C. the polyurethane (I) is slowly dissociated into TDI (II), ethylene glycol (III) and some β-hydroxyethyl chain-ended polyurethane (IV). Free isocyanate reacts with the hydrogen atom of the carbamate group to form allophanate crosslinks (V) which give polyurea (VI) by loss of CO_2.

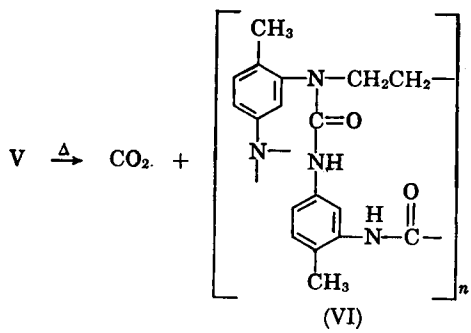
Meanwhile part of the diisocyanate turns yellow; the structure of the colored material is as yet unknown. (IV) gives 2,4-toluenediamine (VII), ethylene oxide, and CO_2. The diamine reacts with TDI to yield the corresponding polyurea (VIII). On prolonged pyrolysis, TDI probably undergoes a catalytic reaction in the presence of degraded products by



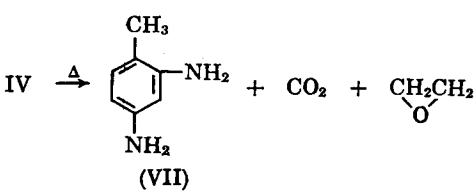
(I) (II) (III) (IV) (1)



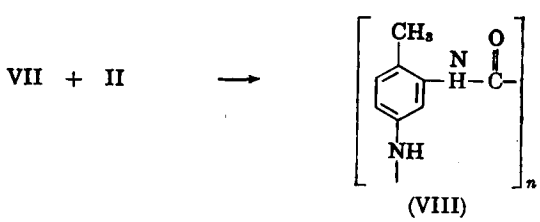
(2)



(VI) (3)



(VII) (4)



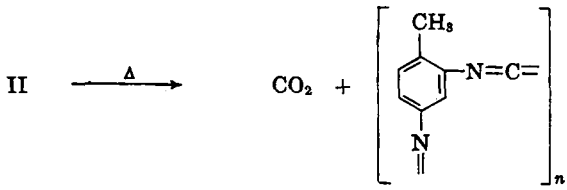
(VIII) (5)

loss of CO_2 to form the unstable dark yellow polycarbodiimide (IX). The latter reacts with ethylene glycol to give the polypseudourea ether (X).

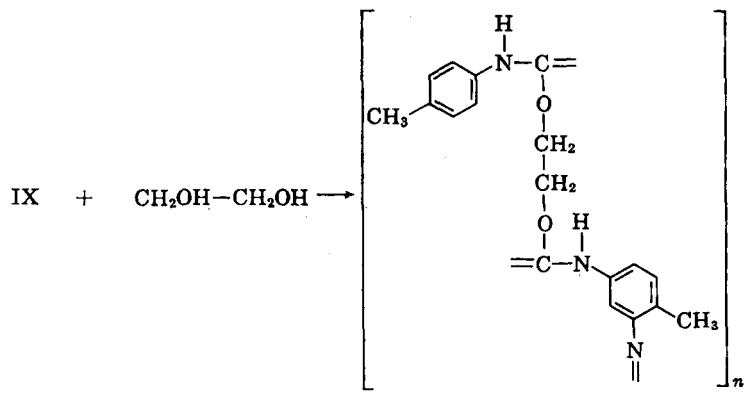
In nitrogen at 200–215 °C. the polymer loses readily CO_2 and turns dark brown very rapidly; the products obtained are ethylene glycol, ethylene oxide, 2,4-toluenediamine, a very small amount of water, and polypseudourea ether.

In oxygen or air, a faster rate of CO_2 evolution was observed after 70 hr. of degradation at 152 °C. It was shown that oxidation occurs to a large extent at the methyl group attached to the aromatic ring and also to the methylene group in ethylene glycol. The oxidation liberates water which reacts with isocyanate to give CO_2, and thus increases the rate of CO_2 formation.

On long thermal treatment or at higher temperature, when the amount of isocyanate liberated was substantial in quantity, the following reactions occurred.



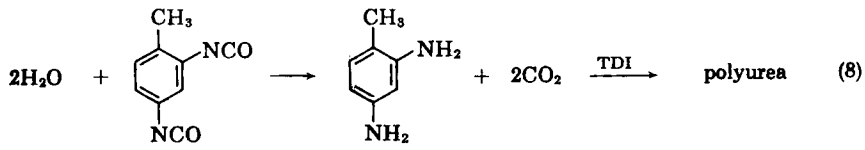
(IX) (6)



X (7)

There was a very small amount of water liberated from pyrolysis. While the import of this is not certain, this might be explained by cyclization from the β-hydroxyethyl carbamate structure as observed in the case of the diphenyl urethane of ethylene glycol.[16] No evidence of the oxazolidone ring was found in the degraded product, due to the interference with the urethane band or to further reaction. The formation of a band at 5.75 μ which could be possibly characteristic of the oxazolidone was observed in the pyrolysis of film. However, it is not possible to speculate further on this reaction at the present.

In oxygen the reaction taking place is that given by eq. (8):



Validity of the Proposed Mechanism

Dissociation into Glycol and Isocyanate. The first step of dissociation was usual in the degradation of urethanes. Isolation of ethylene glycol in the degradation tends to support this dissociation step. Also, .1 degradation of the bisurethane of TDI and ethyl alcohol supported this step, as EtOH was isolated and TDI was shown by the presence of the band at 4.4 μ in the infrared spectrum of the residue isolated after 60 hr.

Formation of Crosslinked Polyurethane. Allophanate formation was observed during degradation of ethyl *N*-phenyl carbamate by Dyer and Wright.[17] Also Kogon[18] showed that aryl isocyanates react with ethyl carbanilate at 125–140°C. to give the ethyl α,γ-diallophanate.

Evidence of Formation of Allophanate-Crosslinked Polyurethane

Reaction of Polyurethane and TDI. TDI reacted almost immediately with polyurethane in presence of triethylenediamine as catalyst at 60–70°C. This showed that TDI was very reactive. The allophanate obtained readily lost 50% CO_2 after 2 hr. at 150–152°C. in nitrogen or oxygen. It was true that triethylenediamine acted as a powerful catalyst for degradation, but still loss of CO_2 without catalyst was important as shown in the following experiment.

Degradation of Linear Polyurethane in Presence of TDI. To 4.720 g. of polyurethane (corresponding to 40 mmoles CO_2) heated at 152–154°C., was added under nitrogen 1 cc. of tolylene diisocyanate, and rate of CO_2 evolved was measured. After 22 hr., 3.2 mmoles of CO_2 (ca. 8%) evolved, while without TDI, after this length of time only 1–2% was collected. The polymer less soluble in THF was washed with anhydrous ether and dried. Its infrared spectrum was similar to that of the residue from polyurethane degraded in pure nitrogen for 310 hr. This fast loss of CO_2 is an evidence for the allophanate formation.

Yellowing of TDI. TDI heated at 150°C. turned very rapidly yellow, then yellow brown. As CO_2 evolved too slowly at 150°C., the yellowing was probably not attributable to the formation of polycarbodiimide. Two identical samples of TDI were put in tubes filled with oxygen and with nitrogen, respectively. After 1 hr. at 155°C. the sample under oxygen turned quite yellow, the sample under nitrogen was less yellow. The color was nearly the same in O_2 or nitrogen after 2 days at 155°C. At 130°C. it took about 20 hr. for TDI to become yellow in nitrogen, while

under ultraviolet radiations, in a closed quartz cell, only 2 hr. was required. The nature of this yellowing is not yet fully understood.

Formation of CO_2 from β-Hydroxyethyl Carbamate. The loss of CO_2 by this process, slow at 152°C., became predominant and rapid at 200–215°C. At high temperature, CO_2 was due to the condensation of TDI to the polycarbodiimide and formation of ethylene oxide from the β-hydroxyethyl carbamate structure.

Polyurea Formation from Diamine and TDI. This step was a normal consequence when amine and isocyanate were present.

Formation of Carbodiimide. The formation of carbodiimide by thermal pyrolysis had already been reported in the literature.[1,19] The formation of polycarbodiimide from tolylene 2,4-diisocyanate was proved by the following experiments.

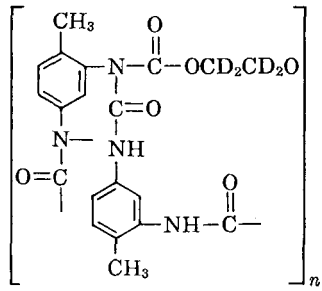
(*1*) Polyurea synthesized from TDI and 2,4-toluenediamine on pyrolysis at 200–210°C. dissociated into amine and isocyanate. TDI lost then carbon dioxide and formed the polycarbodiimide, as shown by the presence of the 4.7–4.75 μ band, in the infrared spectrum of the residue.[4,6]

(*2*) The residue on pyrolysis at 200–215°C. was identified as polypseudourea ether. This supported the fact that at high temperature, the loss of CO_2 by the diisocyanate was much more rapid.

(*3*) TDI heated at 150°C. lost about 10% carbon dioxide after 245 hr.; the infrared spectrum showed a small shoulder at 4.7 μ.

Role of Oxygen in the Thermal Degradation. The role of oxygen was clear when the degradation of crosslinked allophanate polyurethane was studied. Results are shown in Table III. The allophanate polyurethane lost carbon dioxide readily in oxygen or nitrogen at 150–152°C. However, on aging a long time in oxygen atmosphere, an appreciable amount of water was collected, while under nitrogen only a very small amount was obtained. Another crosslinked allophanate polyurethane was synthesized from 2,4-polyurethane and methylene bis(4-phenyl isocyanate). Pyrolysis in oxygen also gave a significant amount of water. In both cases the band at 3.4 μ in the infrared spectra of the degraded products decreased markedly. This marked decrease of the 3.4 μ band was also observed in the residue obtained after the pyrolysis in oxygen of linear polyurethane at 152°C. for 480 hr. In nitrogen this band remained quite sharp. With the exception of this difference, the infrared spectra of the residue were almost identical whether pyrolysis was in oxygen or nitrogen; the band at 6.05–6.1 μ corresponded to the urea structure. Oxygen, therefore, seemed to attack the methyl and the methylene groups with formation of water.

In order to estimate the site of oxidation, a deuterated allophanate polyurethane was obtained from the deuterated d_4-ethylene glycol CD_2OH-CD_2OH and TDI. The crosslinked deuterated allophanate polyurethane had the structural XI:



XI

Degradation of 2.0700 g. (5 mmoles) of the deuterated crosslinked polyurethane in pure, dry oxygen after 248 hr. gave approximately 0.152 g. water containing 19.32% deuterium (analysis by mass spectrometry). Infrared spectrum of the pyrolyzed polyurethane showed an appreciable decrease of the CH_3 band (Fig. 9).

Thus the oxidation occurred at both sites, mostly on the CH_3 group but also at the methylene group. At least 20% of the oxidation took place at the methylene group.

The oxidation of toluene and ethylbenzene was reported to occur by bubbling oxygen in the liquid at 110°C.[20-22] Toluene was reported to be oxidized to benzaldehyde and benzoic acid under the prolonged action of oxygen in the absence of a catalyst. Also, ethylbenzene was oxidized under the same conditions to acetophenone at room temperature or at

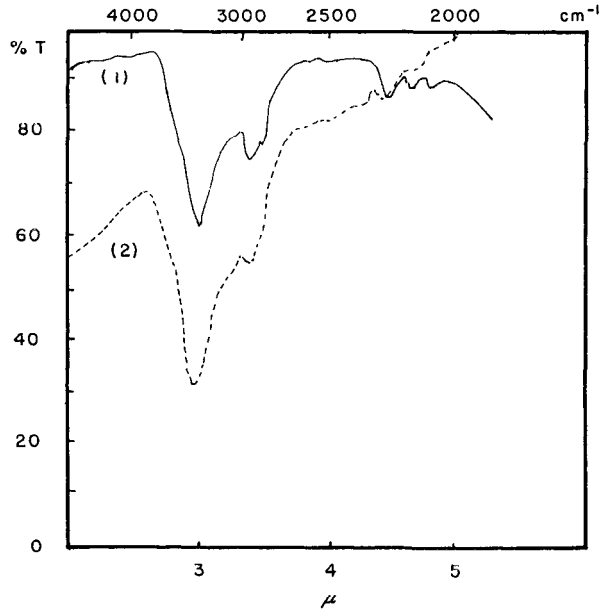


Fig. 9. Variation of absorbance at 3.4μ: (1) deuterated allophanate polyurethane before degradation; (2) the same polymer after degradation in oxygen for 248 hr.

110°C. *m*-Xylene was oxidized at 100°C. to toluic aldehyde and toluic acid.

Recently Engel et al.[23] studied the loss in weight at 175°C. of a polyester urethane synthesized from a polyester glycol and MDI. They found that the loss in weight was about the same in air or in nitrogen. However, no identification of the degraded product was made, although they also observed that the color of the polymer was darker after pyrolysis in air than in nitrogen and attributed that to a probable oxidation of the amine which might be liberated during the pyrolysis. Probably at high temperature the effect of oxygen was masked by a faster rate of degradation in nitrogen.

Color Formation in Polyurethane

The above study makes possible an explanation of the color development in polyurethane. The yellowing in nitrogen at the beginning is due to the yellowing of TDI. In oxygen it is a combination of the yellowing of TDI and the oxidation of the diamine and polyurethane. Later on the formation of polycarbodiimide and polypseudourea ether increases considerably the discoloration. In nitrogen or oxygen at 200–210°C. the color is due mainly to the formation of polycarbodiimide and polypseudourea ether.

In summary, under our experimental conditions, the dissociation of the polyurethane into its components followed by further chemical transformations caused the color development in the polymer.

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Synopsis

The pyrolysis of a polyurethane obtained from tolylene 2,4-diisocyanate and ethylene glycol was studied in nitrogen, air, and oxygen from the double aspect of structural change and color formation. The dissociation of the polymer into its components followed by further reactions liberates diisocyanate, the corresponding diamine, and the polypseudourea ether, as well as other degradation products. The color is attributed to the yellowing of TDI, the oxidation of the diamine, and the presence of the polypseudourea ether.

Résumé

La dégradation de la polyuréthanne préparée à partir du toluène diisocyanate-2,4, et de l'éthanediol a été étudiée au point de vue du changement structural et de l'apparition de la couleur sous atmosphère d'azote, dans l'air et dans l'oxygène. La dissociation du polymère en ses constituants suivie d'autres réactions chimiques libère le diisocyanate et la diamine correspondante, l'éther poly(pseudo)uréique parmi d'autres produits de dégradation. La coloration est attribuée au jaunissement du diisocyanate, à l'oxydation de la diamine et à la présence de l'éther poly(pseudo)uréique.

Zusammenfassung

Die Pyrolyse eines Polyurethans aus Toluylen-2,4-diisocyanat und Äthylenglykol wurde in Stickstoff, Luft und Sauerstoff in bezug auf die auftretende Strukturänderung und Verfärbung untersucht. Die Dissoziation des Polymeren in seine Komponenten und die darauf folgenden Reaktionen setzen unter anderen Abbauprodukten das Diisocyanat, das entsprechende Diamin und den Polypseudoharnstoffäther in Freiheit. Die Farbe wird der Gelfärbung von TDI, der Oxydation des Diamins und der Anwesenheit von Polypseudoharnstoffäthern zugeschrieben.

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