

Stabilization of Polyurethane to Thermal Degradation*

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Synopsis

The labile hydrogen of the carbamate group is primarily responsible for color development in the thermal degradation of polyurethane. Replacement of this hydrogen by an alkyl group prevents back-dissociation. Accordingly, a number of *N*-substituted polyurethanes were prepared, including the methyl, benzyl, benzoyl, acetyl, and the (*N*'-phenylamido) derivatives. Comparative studies at 150–155°C. showed that the *N*-methyl and *N*-benzyl polymers possess outstanding stability under the condition of our testing.

I. INTRODUCTION

It is well known that polyurethanes develop a yellow color on exposure to sunlight or mild heating. A few researches have been carried out directed towards the stabilization of these polymers. To some extent this might be achieved by: (a) the addition of antioxidants or ultraviolet absorbers;^{1,2} (b) the use of a diisocyanate in which an alkylene group separates the isocyanate function from the aromatic ring, thus preventing resonance within the molecule;³ (c) the treatment of polyurethanes with monoisocyanates, ketene, ethylene oxide, or acetic anhydride.⁴

Study of the pyrolysis of the polyurethane obtained from tolylene 2,4-diisocyanate (TDI) and ethylene glycol has shown that in nitrogen, air, or oxygen, the labile hydrogen in the carbamate group favors the dissociation of polymers.

Further reactions cause color formation in the polymer. The nature of the strong coloration of polyurethane in air or oxygen is not completely understood. It appears likely that a great part of the color formed has its origin in the dissociation of polyurethanes under our experimental conditions.⁵ According to our results, color formation could be due to the oxidation of preexisting amino endgroups, followed by further oxidation of amines liberated during the degradation at 150–215°C. and the formation of colored materials such as polypseudourea ether, and an unknown colored substance derived from TDI under heat aging.

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It was demonstrated that the *N,N*-disubstituted carbamates such as the *O*-1-hexadecyl-*N*-propyl-*N*-1-naphthylcarbamate are quite stable to heat aging.⁶ By analogy, replacement of the hydrogen by an alkyl group in polyurethane would substantially decrease the back dissociation and therefore stabilize the polymer against yellowing. This was demonstrated with *N*-methyl and *N*-benzyl polyurethanes, which show a very unusual stability against yellowing.

To prove that the decrease of the dissociation of polyurethane results in an increase in stability of structure and a slow color development of films, substitution of the hydrogen carbamate by various groups was carried on the polyurethane obtained from TDI and ethylene glycol. Polyurethanes containing 0, 50, 75, or 100% *N*-methyl substitution, *N*-acetyl, and *N*-(*N'*-phenylamido)polyurethanes were studied. The *N*-methylpolyurethane was the most resistant to yellowing. *N*-(*N'*-phenylamido)polyurethane and polyurethane containing 75% substitution had about the same extent of coloration. However, the structure of the *N*-(*N'*-phenylamido)polyurethane was largely altered during pyrolysis, while that of the *N*-methyl polymer remained almost intact, as shown by infrared spectra and elemental analyses.

II. EXPERIMENTAL

Synthesis of the *N*-Alkyl Polymers

Dimethylformamide (Matheson Coleman and Bell, b.p. 152–154°C.) was used as solvent due to a greater polarity of the solvent and a greater solubility of the polymer.

Sodium hydride in suspension in oil was used as strong base to abstract the proton from the carbamate group. Subsequent direct nucleophilic displacement on the alkyl halide gave the desired substituted polymer. This was the first alkylation carried with completion directly on polyurethane, though alkylation of urethane by the same way has been known.⁶

***N*-Methyl Polyurethane.** A 500-cc. three-necked flask equipped with condenser, drying tube, nitrogen inlet, dropping funnel, and stirrer was used. The apparatus was flamed outside while swept by nitrogen. A 0.05 mole (2.4 g.) portion of sodium hydride (50% suspension in oil) and 50 cc. DMF was placed in a flask cooled by a sodium chloride-ice bath. A solution of 0.02 mole structural unit (4.72 g.) of 2,4-polyurethane in 50 cc. of DMF was added dropwise to the solution with vigorous stirring. Heat was liberated and hydrogen evolved. If necessary, the ice bath was removed to initiate the reaction. The suspension was then stirred for half an hour at room temperature after addition of the polymer. An excess of methyl iodide (0.05 mole) in solution in 5 cc. of DMF was then added dropwise at room temperature to the reaction mixture, and stirring was continued for another hour at room temperature. On cooling, sodium iodide precipitated from the DMF solution. The volume of the solution after filtration was reduced to 15 cc. by distillation under vacuum

of the DMF. The polymer was precipitated into a large excess of water, filtered, washed many times with warm water, and dried with suction. It was then dissolved in CHCl_3 and decolorized with charcoal until an almost colorless solution of polymer in CHCl_3 was obtained. The polymer dried in vacuum at 60°C . for 1 day, obtained in 75% yield, softened at $105\text{--}110^\circ\text{C}$.

ANAL. Calculated for $(\text{C}_{13}\text{H}_{16}\text{N}_2\text{O}_4)_n$: C, 59.00%; H, 6.05%; N, 10.50%. Found: C, 59.35%; H, 6.15%; N, 10.75%.

The infrared spectrum showed little or no NH band and bands at 3.4, 5.9, 6.25, 6.35, 8.6–8.7, 9.6, 11.2, 12.2, 13, and $13.7\ \mu$.

N-Benzyl-Polyurethane. The same technique as for the N-methyl polymer was used, except that methyl iodide was replaced by benzyl bromide. The substituted polymer was obtained with a yield of 78% and softened at $107\text{--}109^\circ\text{C}$.

ANAL. Calculated for $(\text{C}_{23}\text{H}_{24}\text{N}_2\text{O}_4)_n$: C, 72.12%; H, 5.77%; N, 6.73%. Found: C, 72.20%; H, 6.10%; N, 6.92%.

The infrared spectrum presents bands at 3.3, 3.4, 5.9, 6.2, 6.3, 6.65, 6.9, 7.1, 7.7, 8.2, 8.7–8.8, 9.2, 9.6, 11.2, 12.1, 13, 13.6, and $14.2\ \mu$.

Partially Substituted Polyurethanes. The same technique was used with the exception that the suspension of sodium hydride in DMF was added to the solution of polyurethane in DMF. Polyurethanes of 50 and 75% substitution were prepared. Details are shown in Table I.

TABLE I

	50% substitution	75% substitution
Polyurethane, g.	11.8	23.6
NaH, g.	2.4	7.2
CH_3I , g.	8.0	24.0
Substituted polyurethane, g. ^a	10.2	21.0
Yield, %	81.0	80.0

^a The polymer was weighed after one purification. They were still slightly yellow.

A fraction of each polymer was purified until the procedure gave a perfectly white polymer before being sent for analysis.

ANAL. Calculated for 50% substitution: C, 57.60%; H, 5.60%. Found: C, 57.60, 57.78%; H, 5.78, 5.84%. Calculated for 75% substitution: C, 58.36%; H, 5.83%, Found: C, 58.28, 58.22%; H, 6.10, 5.91%.

N-Acetyl Polyurethane. During the addition of acetyl chloride to the polymer solution, the solution became light yellow, then deep yellow. Repeated purification gave a 54% yield of N-acetyl polymer.

ANAL. Calculated for $(\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_6)_n$: C, 56.25%; H, 5.00%; N, 8.75%. Found: 56.37, 56.25%; H, 5.10, 5.25%; N, 8.96%.

The infrared spectrum shows bands at 2.9 (weak), 3.35–3.4, 5.75–5.85, 6.2, 6.5–6.6, 6.7–7, 7.25 (v.s.), 8–8.2 (broad), 9.2–9.3, 11.5, 12.3, 13, and 13.9 μ .

***N*-(*N'*-Phenylamido) Polyurethane.** Unsubstituted polyurethane (4.7 g.) was dissolved in 50 cc. THF and refluxed. To this were added 0.04 mole of phenyl isocyanate and a few drops of manganese naphthalenate. The solution was refluxed for 3 days. Evaporation of THF and precipitation in ether gave after drying a light yellow powder weighing 5.1 g., decomposing at 171–175°C. with evolution of carbon dioxide. The infrared spectrum shows very strong monosubstitution in the region 13–15 μ . A sample was purified by decolorization with charcoal and sent for analysis.

ANAL. Calculated for $C_{25}H_{22}N_4O_8$: C, 63.29%; H, 4.64%; N, 11.81%. Found: 63.11, 63.51%; H, 4.40, 4.62%; N, 12.00, 11.90%.

Other *N*-alkylation has been tried. The substitution was about 70–80% complete with *N*-benzoyl, *N*-methanesulfonyl, and *N*-allyl polyurethanes. For long-chain alkyl groups, the polymer became a very viscous liquid; purification by the previous method was not successful.

Aging Study

The procedure was already described in another paper.⁵ For color index measurement, each polymer was purified in charcoal and repeated dissolution in $CHCl_3$ and precipitation in *n*-pentane until the polymer solution in $CHCl_3$ became colorless. The color index *I* was defined as

$$I = (T \text{ at } 360 \text{ m}\mu / T \text{ at } 500 \text{ m}\mu) \times 1000$$

where *T* is per cent transmittance.

III. RESULTS AND DISCUSSION

Qualitative Comparative Study of Degradation of *N*-Methyl, *N*-Benzyl, and Unsubstituted Polymers

A solution was made by dissolving 40 mg. of polyurethane in 1 ml. of solvent ($CHCl_3$ for the substituted polyurethane and THF for the unsubstituted polymer). The films were cast on one piece of rock salt under the same conditions: same area, same volume of solution. After 84 hr. at 155°C., the substituted polyurethane turned dark brown. Films cast on glass presented the same phenomenon.

Degradation of *N*-Methyl Polyurethane Powder

From 5.28 g. of polymer (40 mmoles CO_2 theoretically), after 192 hr. of pyrolysis in pure oxygen at 152°C., only 2.3 mmoles of CO_2 (6%) evolved. The polymer was light yellow. The elemental analysis did not change much, however.

ANAL.: Calculated for $(C_{13}H_{16}N_2O_4)_n$: C, 59.00%; H, 6.05%; N, 10.50%. Found before degradation: C, 59.14, 59.35%; H, 6.34, 6.15%; N, 10.75, 10.84%. Found after degradation: 58.99, 59.18%; 6.28, 6.28%; N 10.80, 10.80%.

The infrared spectrum did not change.

Proof of Stability of the Substituted Polymer Under Heat Aging at 152–155°C.

Study on Polymers of Various Degrees of Substitution

It was stated that the yellowing formed during the pyrolysis of nonsubstituted polyurethanes was due to the yellowing of TDI in nitrogen and a combined effect of the yellowing in TDI and oxidation of the free amino endgroups and the amines liberated during the degradation under oxygen.⁵ If this is true, the yellowing should decrease with increase of the amount of *N*-methylation of the unsubstituted polyurethane. The color index *I* was measured in the visible region on polymers containing 0, 50, 75, and 100% *N*-methylation. The result is shown in Figure 1.

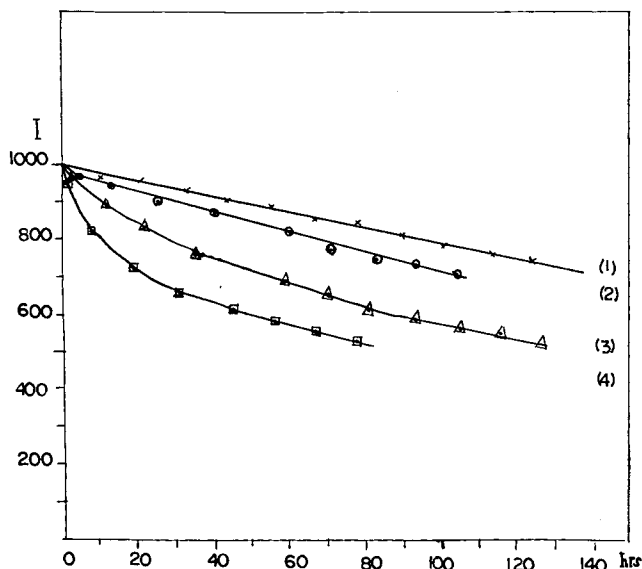


Fig. 1. Color index *I* of polyurethane films: (1) 100% substitution; (2) 75% substitution; (3) 50% substitution; (4) 0% substitution.

*Study of *N*-Acetyl and *N*-(*N'*-Phenylamido)polyurethanes*

It was shown by Wilson⁴ that polyurethane foam treated with monoisocyanates, ketene, ethylene oxide, and acetic anhydride was stabilized to a large extent against yellowing. Monoisocyanates were found most effective. No data were given on polymer treated with acetic anhydride, however. In order to show the unusual stability of the *N*-methylpolyurethane in our experimental conditions, we have studied also the stability of the *N*-acetyl and *N*-(*N'*-phenylamido)polyurethanes regarding their color development and their rate of evolution on pyrolysis. The *N*-acetyl polyurethane is not stable at all, both from the point of view of color development and structural change. It might be speculated that the elec-

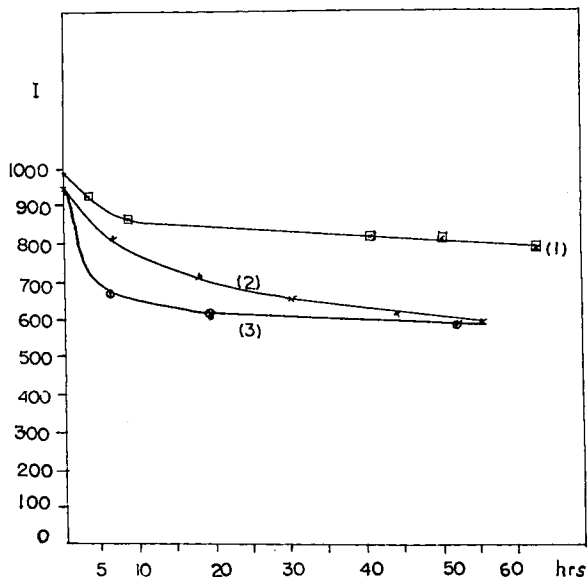


Fig. 2. Color index I of polyurethane films: (1) *N*-(*N'*-phenylamino)polyurethane; (2) unsubstituted polyurethane; (3) *N*-acetylpolyurethane.

tron-withdrawing property of the acetyl group makes the carbamate group less stable. The decrease of yellowing under light reported by Wilson⁴ when polyurethane foam is treated with acetic anhydride would be due to the absence of free amino endgroups in the polymer after reaction with acetic anhydride. The other substituted polymer is as good as the 75% *N*-methyl-substituted polyurethane as regards to its color formation, but its structure changed appreciably during the degradation.

Color Index of the Polymers. The color index of these polymers dropped rapidly at the beginning, then leveled off after a few hours for the *N*-acetylpolyurethane, and about 60 hr. for the other. Results are reported in Figure 2.

Degradation of Polyurethane Powders. Pyrolysis of 3.20 g. *N*-acetylpolyurethane under oxygen at $151 \pm 2^\circ\text{C}$. showed an appreciable loss of CO_2 (32.5% after 11 hr., 53.65% after 89 hr.); 0.101 g. of water was collected. The residue in the flask weighed 2.49 g. (total recovery 3.0 g.) The infrared spectrum of the amber-brown product after pyrolysis showed the appearance and disappearance of numerous bands. The broad urethane band at $5.7\text{--}5.9 \mu$ became narrower. A strong new band at 6μ appeared, indicating probably the amide structure. The bands at 6.9 and 7.1μ fused to one large band absorbing at 7.1μ . The broad band at 9.35μ was replaced by two bands, at 9.7 and 9μ .

The *N*-(*N'*-phenylamido) polyurethane powder degraded under oxygen at 152°C . lost 54.7% carbon dioxide after 189 hrs. From 2,000 g. of polymer, corresponding to a theoretical amount of 8.4 moles of CO_2 , 4.6 moles

of CO₂ evolved, and 98.3 mg of water was collected. The residue in the flask weighed 1.895 g. (total recovery 2.199 g.). The infrared spectrum showed a large decrease of the band at 9.4 μ , accounting for the evolution of carbon dioxide.

We would therefore speculate that the stability of the polyurethane formed by Wilson was due to the reaction of isocyanates, ketene, ethylene oxide, and acetic anhydride with free amino groups expected to be present in foams. This reaction prevents the yellowing by oxidation of free amine.⁷ When monoisocyanates are heated in gas phase or in solution above room temperature for a long time, it might be expected that the isocyanate would react to a certain extent with the hydrogen of the carbamate group as basic catalyst present in polyurethane. This fact explains the better stability of the polymer when treated with isocyanate.

CONCLUSIONS

For the first time direct *N*-alkylation was carried on polyurethane. The *N*-methyl and *N*-benzyl polymers were proved of unusual stability as regards to color formation and structural changes during pyrolysis at 150–155°C. The color intensity decreases with increase in the amount of substitution. *N*-(*N'*-Phenylamido)polyurethane is good regarding its color development; *N*-acetylpolyurethane is quite unstable.

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Résumé

L'hydrogène labile du groupement uréthane est l'agent principal de l'apparition de couleur dans la pyrolyse du polyuréthane étudié dans ce laboratoire. Le remplacement de cet atome d'hydrogène par un groupement alcoyle empêche la dissociation. Un bon nombre de polymères substitués sur l'atome d'azote ont été préparés tels que le *N*-méthyl, le *N*-benzyl, le *N*-benzoyl, le *N*-acétyl, le *N*-(*N*-phénylamido). Le *N*-méthyl et le *N*-benzyl sont les plus stables dans nos conditions expérimentales.

Zusammenfassung

Der labile Wasserstoff der Urethangruppe ist die Hauptursache für die Farbentwicklung bei der in unserem Laboratorium untersuchten Pyrolyse des Polyurethans. Der Ersatz dieses Wasserstoffatoms durch eine Alkylgruppe verhindert die Dissoziation.

Eine grössere Zahl an Stickstoff substituierter Polymerer, wie das *N*-Methyl-, das *N*-Benzyl-, das *N*-Benzoyl-, das *N*-Acetyl- und das *N*-(*N'*-Phenylamido)-derivat wurden dargestellt. Unter den gewählten Versuchsbedingungen sind das *N*-Methyl- und das *N*-Benzylderivat am stabilsten.

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