

# Effect of Structure on the Thermal Stability of Photocurable Urethane Acrylate Formulations

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## SYNOPSIS

The effect of structural segments on the thermal stability of photocurable urethane acrylates was studied. A series of model compounds, where one segment of the molecular structure was varied at a time while keeping the remainder of the molecule unchanged, was tested for thermal stability. The results from this study indicate a prominent equivalent weight effect: Increasing the equivalent weight decreases the thermal stability within a given series of model compounds. Polyol-based urethanes were found to be more stable than their amine counterparts. Of the hydroxy-terminated starting materials, polycaprolactones were found to produce the greatest thermal stability, whereas polyethers resulted in the least stable photocurable materials. The diisocyanate segment exhibits a marked effect on the thermal stability of the cured material also. Surprisingly, the dicycloaliphatic diisocyanates resulted in greater stability than the aromatic diisocyanates, while the monocycloaliphatic diisocyanates yielded the least stable materials in the model compound series tested.

## INTRODUCTION

Radiation-curable coatings are generally prepared from an acrylate or an epoxy functional oligomer, a reactive diluent containing at least one ethylenic function, and a photoinitiator capable of starting the radiation-induced polymerization via free radical or cationic routes. These coatings are faster curing and easier to process than conventional systems and, thus, present considerable economic advantages in addition to their versatility, which allows for a wide range of physical properties and performance characteristics.

Several studies have been undertaken to understand the structure-property relationships of radiation-curable coatings and, in this respect, their thermal stability has received considerable attention in the chemical literature. Recent data shows that electron beam curing results in greater thermal stability than UV curing, which in turn yields greater stability than thermal curing,<sup>1,2</sup> an observation that suggests that the residual photoinitiator plays a role

in the thermal degradation of the cured polymer. The thermal stability of the cured polymer has also been related to specific structural features within the molecule. Isocyanurates, for example, are reported to be more stable than oxazolidones, which are more stable than urethanes.<sup>3</sup> Polyesters are reported to have superior stabilities compared to polyethers,<sup>4</sup> and the relatively high stability of bisphenol-A-based polymers is attributed to the possible antioxidant effect of the phenol moiety, which possibly functions as a free radical scavenger.<sup>5</sup>

Parasubstituted aromatic diols when used as chain extenders in polyurethane synthesis impart greater thermal stability to the cured material than their orthosubstituted counterparts.<sup>6</sup> Parasubstituted aromatic diisocyanates such as diphenylmethane diisocyanate (MDI) were also reported to yield more stable polyurethanes than the orthosubstituted tolylene diisocyanate (TDI), presumably due to the formation of the thermally stable polycarbodiimides from the MDI residues as compared to the more volatile polyureas formed from the TDI residues.<sup>7</sup> Saturated MDI-based coatings, which lack the resonance stabilization of the aromatic rings, do not show the thermal stability exhibited by their MDI counterparts.<sup>8</sup>

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Factors affecting the thermal stability of the urethane segment of radiation-curable polymers have also been investigated. For example, the catalysts used in the synthesis of the polyurethane segment have been reported to enhance the thermal degradation of the cured film. A study of a series of catalysts showed that the use of nickel naphthenate yields the most stable oligomers. The stability decreases in the following order: nickel naphthenate > zinc naphthenate > zinc octoates > tributylamine > dibutyltin dilaurate.<sup>9</sup> It is noteworthy that organotin salts, which are the most frequently used catalysts in urethane synthesis, appear to reduce the polymer's thermal stability. As expected, the thermal stability decreases with increasing organotin catalyst concentration.<sup>10</sup>

An early study of the thermal stability of polyurethanes and polyureas indicated that *N*-methyl substituted amines yield more stable polymers than the corresponding unsubstituted amines.<sup>11</sup> Later work, however, has shown that *N*-alkyl substitution of an aryl urea results in the most significant lowering of thermal stability.<sup>12</sup> Our work, reported in this article, may shed some light on this issue. We have found that the equivalent weight of the oligomer is a factor of such magnitude that it may mask other effects such as chain branching. To discern differences due to structural factors, polymers of similar equivalent weights must be compared. The effect of equivalent weight did not go unnoticed by other investigators. Manning<sup>13</sup> observed that the rate of depolymerization increases directly with increasing molecular weight of the polymer.

The thermal degradation of radiation-curable polymers represents a complex kinetic situation arising from multiple initiation steps at random scission sites, depolymerization, termination, and chain transfer.<sup>13</sup> The situation is further complicated by oxidative reactions in the presence of oxygen, and the effects of residual photoinitiators and urethane catalysts, and other factors such as the molecular symmetry of the chain extender<sup>8</sup> and its molar concentration in the polymer chain.<sup>14</sup> In general, thermal degradation of polyurethanes involves an initial stage where trapped volatile materials are released<sup>14</sup>; this is followed by the scission and depolymerization, resulting in weight loss and degradation of mechanical properties, and finally a complete thermal breakdown of the chain to yield a mixture of simple hydrocarbons, CO, CO<sub>2</sub>, HCN, MeOH, acrylonitrile, and acetonitrile.<sup>15-18</sup>

The heat aging weight loss experienced by almost all UV-cured coatings is highly dependent on the components of the formulation and composition of

each component. This formulation effect is demonstrated in Figure 1, which depicts the varying degrees of weight loss demonstrated by several commercial coatings. We conducted this study on cured films using thermogravimetric analysis at 200°C in air atmosphere. Weight losses in air arise from a combination of thermodynamic (bond scission) and oxidative degradation. In an attempt to determine the mechanistic origins of these weight losses, selected coatings were also tested in pure nitrogen atmosphere to identify the losses due to thermodynamic instability alone. The data gathered in this experiment shows that while some formulations are stable toward both oxidative degradation and thermal decomposition (Fig. 2), others are more susceptible to oxidative degradation, as represented in Figure 3.

The nature of the components present in a formulation is clearly the most important factor affecting the thermal stability of a given coating. This effect is further illustrated in Figure 4, which depicts the heat-aging weight loss of films prepared from two different commercial oligomers. The films were prepared from oligomer-photoinitiator blends in the absence of monomers or other additives to isolate the effect of the oligomer on the cured film's thermal stability. The study confirms that high molecular weight species such as oligomers exhibit varying degrees of thermal stability, directly related to their backbone structure.<sup>19</sup>

It must be pointed out, however, that the initial weight loss exhibited by a UV-curable coating, usually in the range of 2-6%, is the result of vaporization of low molecular weight components present in the film, and should not be attributed to thermal instability. To illustrate this, we aged three different

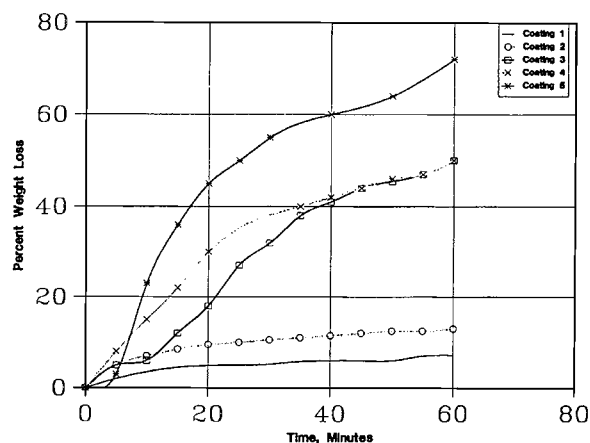
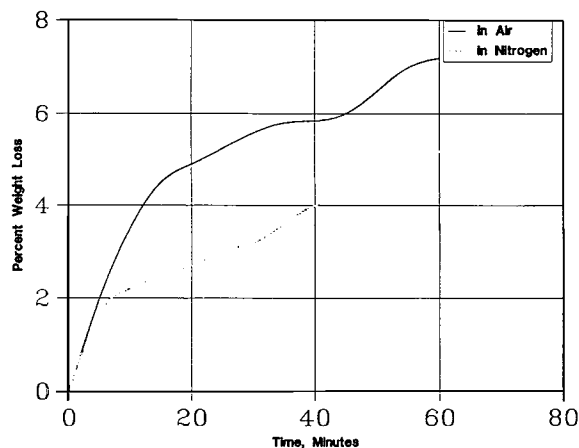


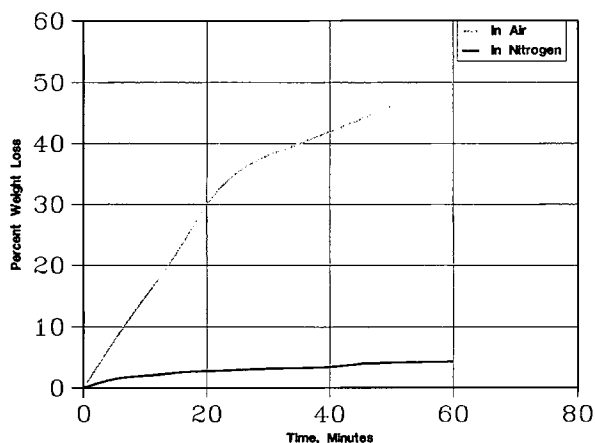
Figure 1 Heat-aging Weight Loss of Commercial Coatings at 200°C.



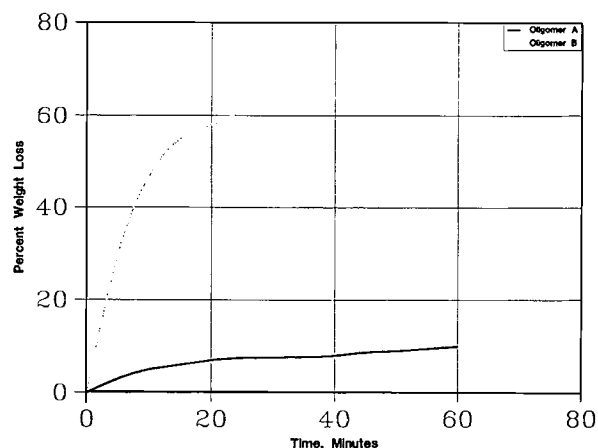
**Figure 2** Heat-aging Weight Loss of Coating 1 in Air and in Nitrogen at 200°C.

coatings at 200°C for 40 min in closed vials. The head space was then analyzed by gas chromatography-mass spectrometry using the purge-and-trap technique. In one case, the major heat-aging product was found to be residual photoinitiator, in the second case the major product was unreacted low molecular weight monomer, while the third coating yielded a mixture of monomer and photoinitiator as the initial heat-aging products.<sup>20</sup>

Our literature survey revealed that, while certain components of UV-curable coating formulations have been studied,<sup>21</sup> no comprehensive investigation of the segmental components of the oligomers has been reported. The work reported in this article represents a systematic approach to identify the structure-property relationships of specific segments and components that may contribute to the thermal aging characteristics of UV-curable coatings.



**Figure 3** Heat-aging Weight Loss of Coating 4 in Air and in Nitrogen at 200°C.



**Figure 4** Heat-aging Weight Loss of Oligomers A and B at 200°C.

## EXPERIMENTAL

This section describes the generalized experimental conditions under which the studies were conducted. Generalized experimental conditions are used for the sake of brevity since the number of model oligomers and formulations is extensive. Representative procedures for model oligomer synthesis, prototype formulation, cure conditions, and thermal aging evaluations will be presented.

### General Oligomer Synthesis

A 2-L, four-neck flask was equipped with a thermometer, a mechanical stirrer, a reflux condenser, a gas inlet tube, and a pressure-equalized dropping funnel. The isocyanate-containing component of the oligomer was weighed into the flask. Dibutyltin dilaurate (0.03% by weight), a suitable thermal polymerization inhibitor such as butylated hydroxytoluene (0.03% by weight), and a diluent monomer (25% by weight) were introduced into the flask, and the contents were stirred under a blanket of dry air until uniformly mixed.

The stoichiometric amount of 2-hydroxyethyl acrylate, necessary to react with one half of the isocyanate functionality, was added to the mixture dropwise at a rate sufficient to maintain a temperature between 25–35°C. The addition usually required between 10–20 min, and in some cases required the use of an external cold water bath to cool the contents of the flask to the prescribed temperature. After the addition was completed, the mixture was stirred at room temperature for an additional 1 to 2 h to ensure complete reaction.

The prepolymer containing the functional group

**Table I Model Compounds for the Amine Structure Study**

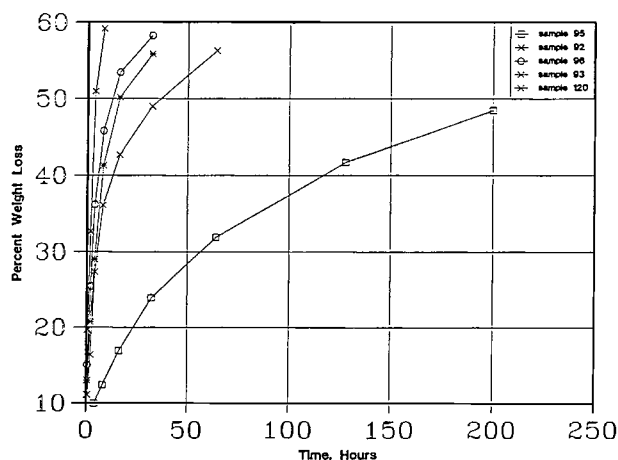
Sample	Prepolymer Type	Functionality	Branch Site	Viscosity (mPa s)
4024-92	Homopolymer	Trifunctional	Glycerine	7,040
4024-93	Homopolymer	Trifunctional	Glycerine	19,240
4024-95	Homopolymer	Trifunctional	Trimethylolpropane	Semisolid
4024-96	Homopolymer	Difunctional	Unbranched	8,680
4024-120	Copolymer	Difunctional	Unbranched	6,540

was added to the reaction mixture in an amount calculated to consume the remaining isocyanate functionality. This dropwise addition was regulated at a rate sufficient to maintain the reaction temperature below 55°C. The mixture was stirred under an atmosphere of air until all the isocyanate was consumed, as indicated by infrared analysis. In certain cases, the reaction mixture was heated to 70°C to complete the reaction.

The resulting oligomer-monomer solution was stored in sealed, lined cans and was allowed to reach thermal equilibrium at 25°C before its Brookfield viscosity was measured.

### Formulation

Each oligomer was mixed with the calculated amount of reactive diluent and photoinitiator required to yield a liquid coating containing 25% diluent and 3% photoinitiator by weight of the total formula. The mixtures were stirred, and heated to 60°C whenever necessary, until clear homogeneous solutions were obtained.



**Figure 5** Effect of Amine Structure on Heat-aging Weight Loss at 200°C.

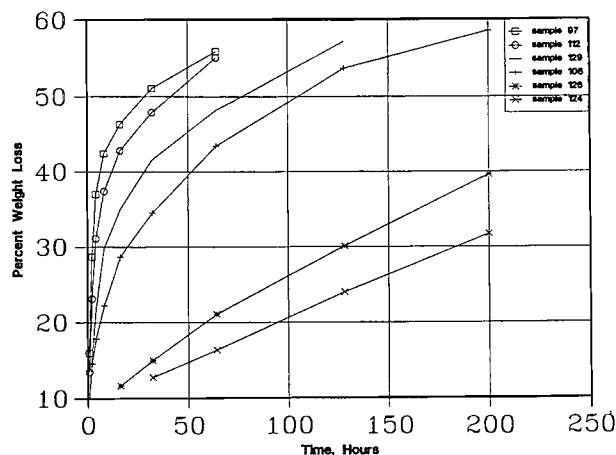
### Testing

Films of each coating were drawn on glass substrates using a 3 mil (76 microns) Bird bar. The films were then cured under a 300 w/in D lamp in air using a conveyerized Fusion Systems curing unit. Cure doses were determined for each coating by plotting the dose vs. modulus curves and identifying the dose required to reach maximum modulus. These doses varied from 0.20 J/sq cm to 2.0 J/sq cm as a function of the coating's composition. To ensure that the films were completely cured, control samples were cured using an electron beam at doses of about 3.0 megarad, and the mechanical properties of the UV-cured systems were compared to these controls. In all cases, the films were shown to be completely cured prior to thermal aging tests. This is an essential step in the experiment since undercured films can easily confound the thermal aging weight loss results by outgassing volatiles and unbound molecular fragments.

The heat-aging tests were conducted in circulating air ovens kept at 125 and 200°C. Samples, two square inch each, were cut from cured drawdowns and then placed on clean glass slides and the initial weight was recorded. The weight of the slide-film combination was recorded after specific intervals at a given temperature in the circulating air oven, and weight loss was plotted vs. time as shown in the preceding figures.

**Table II Model Compounds for the Polyol Structure Study**

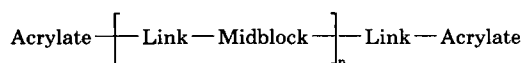
Sample	Prepolymer Type	Oligomer Viscosity (mPA s)
4024-97	Polypropylene oxide	3,856
4024-106	Polybutylene oxide	6,100
4024-112	Ether copolymer	7,120
4024-124	Polycaprolactone	10,340
4024-126	Polycarbonate	36,000
4024-129	Polyethylene oxide	3,176



**Figure 6** Effect of Diol Structure on Heat-aging Weight Loss at 200°C.

## RESULTS AND DISCUSSION

Radiation-curable oligomers can be generally described as structures in which acrylate termini are linked to a midblock through a distinct molecule or functional group. Generically, these oligomers may be conceptualized as follows:



The links and midblocks can be independently varied. For example, the link may be a urethane group or a urea group, associated with a unique molecular structure, while the midblock may contain polyesters, polyethers, polycaprolactones, polysiloxanes, polyalkylenes, or copolymers containing these moieties. Thus, a myriad of oligomeric structures is possible with each structure possessing its own unique characteristics, mechanical properties, and thermal stability.

To isolate the effects of each specific segment, our approach involved the synthesis of several series of model oligomers. Each series represented a set of oligomers in which one structural segment was var-

ied while the remainder of the molecule was maintained unchanged.

Thermal aging weight loss was selected as the criterion for comparing film stabilities because of the ease, efficiency, and precision of this method. Other test criteria, such as changes in the static and equilibrium moduli, or other dynamic mechanical properties were deemed too time consuming to be suitable for a study of this magnitude.

## Structural Effects

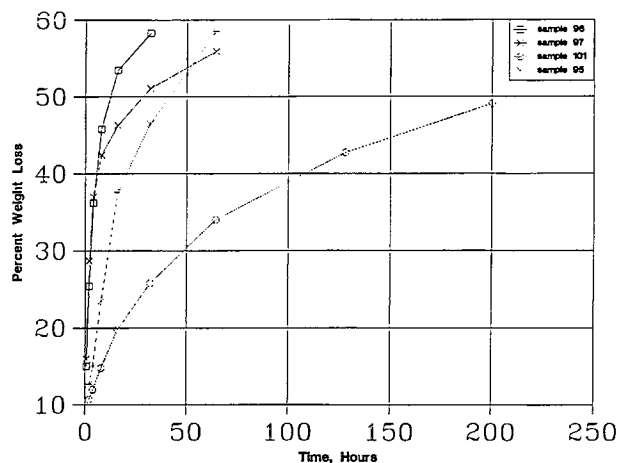
### Effect of the Amine Structure

The study was begun with variations in the midblock molecular segment. These segments are based on commercially available starting materials, usually in the form of end-functionalized prepolymers. A commonly used prepolymer is the amine-terminated polypropylene oxide, available in both di- and trifunctional forms (Texaco Chemical Company). Amine-terminated copolymers of propylene and ethylene oxides are also available. A series of oligomers based on these prepolymers were synthesized by coupling the midblock section to an acrylate function through a diisocyanate linking group. This sequence provided oligomers with urea linkages as a common feature but variable in the type of amine backbone and functionality. The details of this series appears in Table I.

Figure 5 details the thermal aging weight loss at 200°C for cured films prepared from the amine oligomers described in Table I. The data reveals considerable weight loss for both the homopolymer- and the copolymer-based films. The effect of the backbone appears to be most significant, with trimethylolpropane-based oligomers exhibiting the least weight loss on heat aging. The data also shows that difunctional amines produce less stable oligomers than their trifunctional counterparts, perhaps due to the tighter, more crosslinked network that results from trifunctional reactants.

**Table III** Model Compounds for the Link Functional Group Study

Oligomer Code	Prepolymer Midblock	Prepolymer Functional Group	Prepolymer Functionality	Oligomer Link	Oligomer Viscosity (mPa s)
4024-95	PPO	Amine	3	Urea	Semisolid
4024-101	PPO	Hydroxyl	3	Urethane	362,400
4024-96	PPO	Amine	2	Urea	8,680
4024-97	PPO	Hydroxyl	2	Urethane	3,856



**Figure 7** Comparison of the Effects of Polyols and Polyamines on Heat-aging Weight Loss at 200°C.

### Effect of the Diol Structure

Another structure commonly used as a midblock segment is the class of hydroxy-terminated prepolymers. These prepolymers are available in a variety of polymeric backbones, allowing for a direct comparison of structural features. In this study, several difunctional hydroxy-terminated polyethers and polyesters were examined as segments in urethane acrylate oligomers. To eliminate all but backbone effects, the molecular weight of each reactant was controlled so that all members of the series possessed similar equivalent weights. The details of this series appears in Table II.

Heat-aging weight loss for this series at 200°C is depicted in Figure 6, which shows a distinct order of thermal stability as follows: polycaprolactone > polycarbonate > polybutylene oxide > polyethylene oxide > ether copolymer > polypropylene oxide.

Comparison of this series with the diamine series discussed previously reveals that polyol-based oligomers are slightly more stable than their polyamine-based counterparts. This effect of the "link" functional group is examined further in the following study.

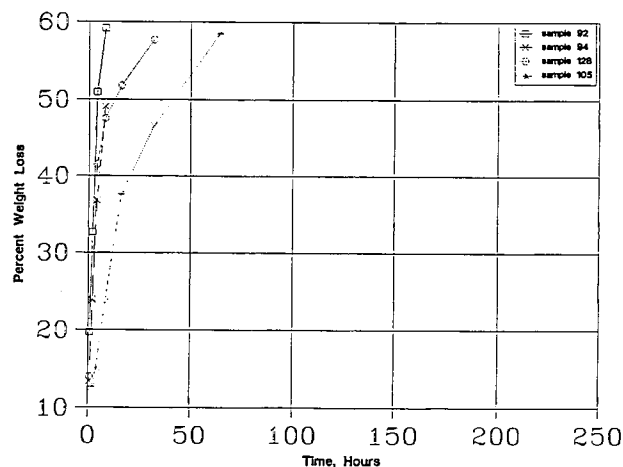
### Effect of the Link Functionality

To more closely examine the link group effect implied in the previous study, a controlled experimental design was planned. The design was based on polypropylene oxide midblock prepolymers that were either hydroxy- or amine-terminated di- or trifunctional compounds, and the midblocks were tied to the acrylate end groups through the same diisocyanate structure. Details of this study are summarized in Table III.

Heat-aging weight loss at 200°C as a function of time is plotted for this series in Figure 7. Examination of the plot shows that the least stable model compound is 4024-96, which is based on the diamine-terminated prepolymer. The most stable model compound in the series is 4024-101, which is based on the diol-terminated prepolymer. In both the di- and the trifunctional cases, amines always produced less stable coatings than their polyol counterparts. It is interesting to note that the trifunctional prepolymers produced more stable films than the difunctional materials despite the higher molecular weights of the trifunctional model compounds. Increasing the molecular weight is expected to decrease thermal stability by increasing the statistical availability of degradation initiation sites. However, an increase in both the molecular weight and the functionality may result in shorter chains and, therefore, diminished susceptibility to degradation. Thus, it is the equivalent weight, rather than the molecular

**Table IV** Model Compounds for the Diisocyanate Structure Study

Oligomer Code	Midblock Group, Functionality	Diisocyanate Type	Diisocyanate Structure	Oligomer Viscosity (mPa s)
4024-92	Amine, 3	Cycloaliphatic	Monomeric	7,040
4024-94	Amine, 3	Dicycloaliphatic	Monomeric	35,960
4042-105	Amine, 3	Aromatic	Polymeric	69,000
4042-128	Amine, 3	Aromatic	Monomeric	Semisolid
4039-21	Hydroxyl, 2	Cycloaliphatic	Monomeric	11,580
4039-58	Hydroxyl, 2	Cycloaliphatic	Monomeric	12,680
4039-60	Hydroxyl, 2	Dicycloaliphatic	Monomeric	28,520
4039-68	Hydroxyl, 2	Aromatic	Monomeric	8,080
4039-76	Hydroxyl, 2	Aromatic	Monomeric	53,360
4039-78	Hydroxyl, 2	Aromatic	Polymeric	284,800



**Figure 8** Effect of the Diisocyanate Segment and Amine-terminated Prepolymer on Heat-aging Weight Loss at 200°C.

weight, of the oligomer that affects the thermal behavior of these model compounds of radiation-curable coatings.

#### **Effect of the Link Group Molecular Structure**

A variety of diisocyanate structures are available for use as link groups in urethane acrylate coating formulations. To study the effects of diisocyanates and the wide spectrum of potential features afforded by these systems, we examined the series of model compounds described in Table IV.

Results for this series are plotted in Figures 8 and 9 for cured films aged at 200°C. Figure 8 depicts the first design phase, that using amine-terminated prepolymers as the constant midblock structure, while Figure 9 represents the portion of the experimental design where the midblock structure was hydroxy-terminated prepolymer.

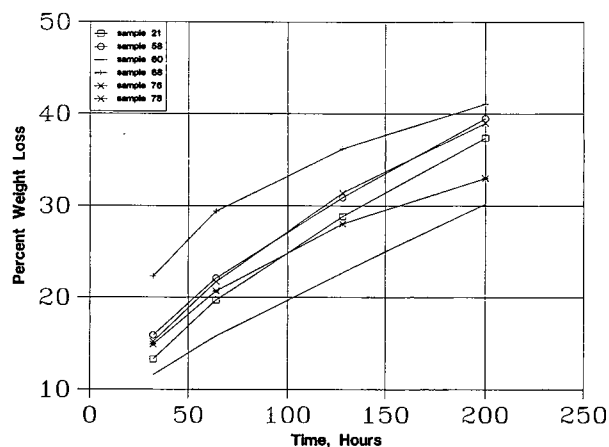
While there appears to be some crossover points in specific cases, the two plots generally agree. The cycloaliphatic diisocyanates seem to be the least favored choice for thermal stability in each study. On the other hand, the dicycloaliphatic diisocyanates appear to impart the greatest thermal stability to the cured films. A surprising result is that the aromatic diisocyanates fall somewhere between the aliphatics in both studies. The two studies show conflicting results when comparing the effects of monomeric and polymeric diisocyanates. In the amine-terminated prepolymers series, the polymeric diisocyanate shows greater stability than its monomeric counterpart (sample 4024-105 vs. 4024-128), while the reverse trend is observed in the hydroxy-terminated series (sample 4039-76 vs. 4039-

78). This apparent disparity suggests that the effect of the midblock is more significant than the effect of the linking group structure.

#### **Effect of Prepolymer Molecular Weight**

The functional group study presented the second occurrence of an implied molecular weight effect. The first occurrence appeared in the study of amine-terminated prepolymer structures (Table I). To clearly isolate the molecular weight effects, the model compound series described in Table V was tested. The series included di- and trifunctional oligomers based on amine-terminated polypropylene oxide. The series members varied in molecular weights, but all other features were maintained. As in all the previous studies, the midblocks were connected to the acrylate end groups through a diisocyanate molecule that results, in this case, in urea links for all members of the series.

The cured film thermal aging weight loss results, shown in Figure 10, indicate the strong effect of the molecular weight on thermal stability. An increase in the molecular weight, without changing the functionality, leads to a decrease in thermal stability. Naturally, the trend is apparent for both the di- and trifunctional prepolymers. But increasing the functionality (i.e., decreasing the equivalent weight) within a given set of model compounds increases the thermal stability by reducing chain length. This effect is best shown by comparing sample 4042-92 (MW 5000, EW 1667) to sample 4042-109 (MW 4000, EW 2000). The former is marginally more stable than the latter despite the higher molecular weight of 4042-92.



**Figure 9** Effect of the Diisocyanate Segment and Hydroxy-terminated Prepolymer on Heat-aging Weight Loss at 200°C.

**Table V Model Compounds for the Molecular Weight Study**

Sample Code	Prepolymer Functionality	Approximate Prepolymer Molecular Weight	Oligomer Viscosity (mPa s)
4024-92	3	5,000	7,040
4024-93	3	3,000	19,240
4042-109	2	4,000	4,660
4042-96	2	2,000	8,680
4042-103	2	400	302,000
4042-104	2	230	515,200

## SUMMARY

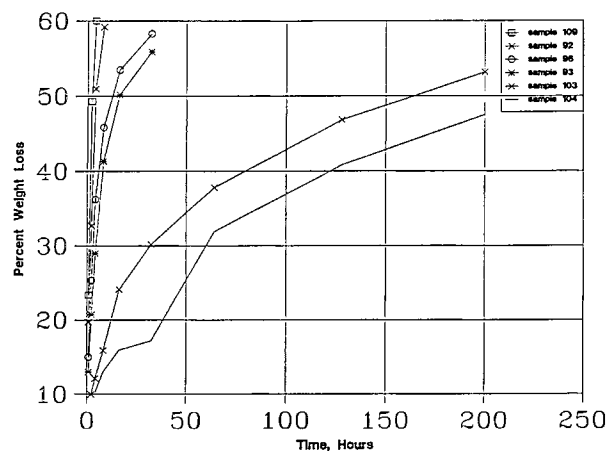
The thermal stability of UV-curable coatings is a function of the components present in the formulation. The oligomer structure, the type of diluent, and the nature (as well as the amount) of the photoinitiator used all affect the thermal stability of the cured coating.

The oligomer, which usually represents the major component in the UV-curable coating formulation, appears to be the most important factor affecting the thermal stability of the cured coating. This study has examined the effect of various structural segments on the thermal stability of model oligomer compounds, with the following results:

1. Polyol-based oligomers are more stable than their polyamine-based counterparts.
2. Difunctional amines and diols lead to less stable compounds than those derived from trifunctional amines and triols.

3. The diisocyanate segment leads to the following order of increasing thermal stability: dicycloaliphatic > aromatic > cycloaliphatic.
4. The stability of the midblock segments decreases in the following order: polycaprolactone > polycarbonate > polybutylene oxide > polyethylene oxide > ether copolymers > polypropylene oxide.
5. Increasing the molecular weight of the prepolymer decreases the thermal stability of the cured coating. However, increasing the functionality tends to increase the thermal stability. Thus, it is the equivalent weight of the structural segments within the prepolymer that affects its stability. The greater the equivalent weight, the poorer the thermal stability.

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**Figure 10** Effect of Prepolymer Molecular Weight on Heat-aging Weight Loss at 200°C.

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