

## *Polymers*

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*In celebration of the 60<sup>th</sup> birthday of Dr. Andrew K. Galwey*

# **THERMAL STABILITY ENHANCEMENT OF POLYURETHANES BY SURFACE TREATMENT**

*J. H. Flynn<sup>a</sup> and Z. Petrovic<sup>b</sup>*

<sup>a</sup>Scientific Thermal Research and Data Analysis (STRDA) 5309 Iroquois Road, Bethesda, Maryland 20816, USA

<sup>b</sup>Department of Polymer Science and Engineering University of Massachusetts, Amherst, Massachusetts 01003, USA

### **Abstract**

Both oxidation and methoxymethylation of the surfaces of a series of MDI (methylene diphenyl isocyanate) and TDI (toluene diisocyanate) polyether and polyester soft segment 1-4 butanediol polyurethanes result in increased thermal stability as measured by TG. Explosive loss of mass above the hard segment melting temperature suggests that the diffusion of the dissociated diisocyanate moiety is hindered at lower temperatures. Thus suppression of the depolycondensation reaction by chemical blockage of the surface may result in a material with an increased service life at use temperatures as thermal stability of a polyurethane may depend upon the low diffusivity of its diisocyanate comonomer. The effect of vacuum, oxygen and water vapor on the kinetics of mass-loss of several of the polyurethanes is presented.

**Keywords:** diffusion, mass-loss kinetics, polyurethanes, surface blockage, thermal stability, TG

### **Introduction**

The diffusion of reactants such as water and oxygen into, and volatile products out of, the surface of polymeric materials may be the critical and rate-controlling step in their thermal, oxidative, photochemical or hydrolytic degradation at service conditions. Also, the diffusion of antioxidants and stabilizers out of processed polymers contributes to their decreased stability. Such

diffusion process are not easily amenable to definitive experimental measurement or theoretical modeling.

The treatment of a polymeric material which results in decreasing the ability of material to diffuse through its surface regions may improve its lifetime and durability. Here we describe the effects of modification of the surface of polyurethanes by reaction with oxygen and by methoxymethylation of surface NH groups upon their thermal stability at accelerated conditions. Other thermogravimetric evidence for diffusion limited degradation is also presented. (A summary of this work has been published in an American Chemical Society Meeting preprint [1].)

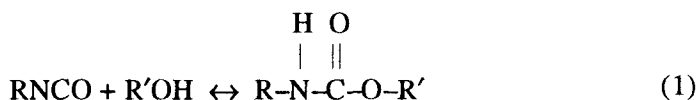
The protection of the surface of materials with a tough impenetrable film is the *raison d'être* for the paint and coatings industry. However, coatings may chip, flake or scratch, or, for many other reasons, be impractical as a protection against deterioration of the substrates beneath them. The diffusion of corrosive materials into a polymer substrate, as well as the diffusion of stabilizers, antioxidants, or even dissociation products from it, can be a major cause for the substrate's deterioration. This problem has been addressed in one way by Frisch [2] who has incorporated film-regenerating precursors into the bulk of a polymer from whence they may diffuse rapidly to the surface and repair a breach in the surface layer. We use another approach here by attempting to incorporate chemical groups in the surface which will slow the diffusion into and out of the substrate. A distribution of chemical groups, incorporated over a broad surface layer, has an inherent superiority over a coating in that the former will not scratch or chip and there are no discontinuous boundaries in which stresses can concentrate.

Oxidation has often been employed to improve the surface properties of polymeric fibers, such as wettability and electrical conductivity. More recently, surface oxidation of high modulus fibers has been employed to improve cohesion and binding to silane coupling agents in composites. Some evidence for the feasibility of an oxidized layer as a diffusion barrier is described in this paper. The methoxymethylation of amide groups with formaldehyde and methanol has been utilized for many years. Here we have found that surface methoxymethylation of polyurethanes causes a marked improvement in their stability as measured by initial mass-loss at a heating rate of two deg/min. The possibility that the thermal stability of a polyurethane may be related to the bulkiness and, therefore, a low rate of diffusion of its diisocyanate comonomer is also suggested.

Polyurethanes are ideal substrates upon which to initiate investigations of the effects of surface blockage upon their thermal stability. They have low ceiling temperatures and they depolycondense into comonomers [3-5]. Grassie

[6–7] has shown that polyurethane bonds are unstable at 170°C and that depolycondensation is the primary degradation reaction. Our experiments indicate that mass-loss occurs at temperatures as low as 150°C at very slow heating rates of 9 degrees/day in nitrogen, air and vacuum [8]. The diisocyanate moiety is large and bulky, and its diffusion out of the polymer, especially at low temperatures, is quite slow and can be easily hindered. Many polyurethanes maintain their integrity to relatively high temperatures since the clusters of hard segments which act as macroscopic cross links do not melt until above 200°C at which temperature degradation is already taking place at a measurable rate.

Even more importantly, the polycondensation – depolycondensation reaction for the breaking of the diisocyanate linkages in polyurethanes has been found to be reversible, i.e.,



As is described in the Experimental Section below, diisocyanates and alcohols react rapidly in the absence of any catalyst at temperatures as low as 100°C to form the urethane linkage. Grassie [6, 7] has found from IR spectra that the urethane linkage disappears upon heating and will reform upon cooling (if further degradation is not effected). Therefore a surface diffusion barrier will produce a 'macroscopic cage effect' within the bulk of the polymer. That is, the build up of an interior pressure of the diisocyanate moiety will shift the equilibrium further in the direction of reformation of diisocyanate linkages. This is the reaction direction already favored at temperatures below the ceiling temperature.

One caveat to the conclusion derived from the experimental results described herein should be noted. Predictions of service life at lower temperatures from rate constants obtained at higher temperatures are seldom found to be quantitatively accurate. This is definitely the case when the temperature extrapolation range passes through the ceiling temperature and/or temperatures of phase changes in the polymer [9]. However both of these effects should result in lifetime prediction errors in the direction of less rather than greater stability. In any event, often one can successfully estimate the rank of relative stabilities of diversely treated polymers from such accelerated data (as we attempt to do in this paper).

## Experimental

Two polyurethanes were used in the methoxymethylation experiments. They were prepared from methylene bis(4-phenylisocyanate) (MDI), 1,4 butanediols

and differing percentages of polytetramethyleneglycol (POLYMEG 2000) soft segment. C1 contained 20% and C3, 50% soft segment. The synthesis and properties of these samples were described earlier [10]. They were methoxymethylated using the technique of Arakawa *et al.* [11]. A mixture of 75 g of paraformaldehyde, 75 g of methanol and 0.1 g of potassium hydroxide was stirred at 60°C until it became a clear liquid. Then 6 g of anhydrous oxalic acid was added as a catalyst. The polyurethane films were submerged in this reaction mixture at 30°C, without stirring, for 24 hours with one series and for 7 days for the other. The treated samples were washed with distilled water and dried in a vacuum at 40°C. A TA Thermal Analyzer 1090 with a 951 electrobalance was used to measure their mass-loss at a heating rate of 2 deg·min<sup>-1</sup>. Infrared measurements were performed with a Specord spectrophotometer with an ATR attachment.

A number of MDI and 2,4-toluenediisocyanate(TDI)-1,4 butanediols with various polyether and polyester soft segments were synthesized by the prepolymer technique (without catalysts) at 100°C. The temperature of the mixture was controlled to counteract self heating and thus to minimize side reactions. These polymers were used in the TG experiments in air, nitrogen, water vapor and vacuum. The thermogravimetric instrument which was used in these later experiments was designed and built at the National Bureau of Standards and is described on pp 226–227 of Ref. [12]. Its internal furnace allows the fast response necessary for quick establishment of isothermal temperatures, and it has sufficient thermal inertia to maintain the isothermal temperature to within one degree. It has been used successfully at heating rates from 0.0001 to 0.1 deg·sec<sup>-1</sup>.

## Results and discussion

### *Surface methoxymethylated polyurethanes*

ATR infrared spectroscopy of the untreated and treated samples indicated that substitution reaction in the NH group had taken place. Since the reaction took place mainly in the surface layers, a degree of substitution could not be calculated. Figs 1 and 2 show the mass-loss curves at a heating rate of 2 deg·min<sup>-1</sup> in nitrogen for the untreated, one day treated, and seven days treated samples C1 and C3, respectively. These methoxymethylated polyurethanes show an enhanced stability during the early stages of the mass-loss reaction. The temperatures at which mass-losses of 5, 10, 15 and 20% were reached are given for C1 (20% soft segment) in Table 1(a) and for C3 (50% soft seg-

ment) in Table 1(b). The samples treated for one day have higher temperatures for mass-loss (are more stable) than those treated for seven days. The improved stability of about 20 degrees for these early stages of degradation, during which the diisocyanate moiety is escaping, points toward a considerably increased service lifetime for these treated samples. The decrease in stability at greater than 50% mass-loss for the treated samples is not relevant here as the material loses its useful properties long before then and no longer contains polyurethane linkages at such an advanced degree of degradation.

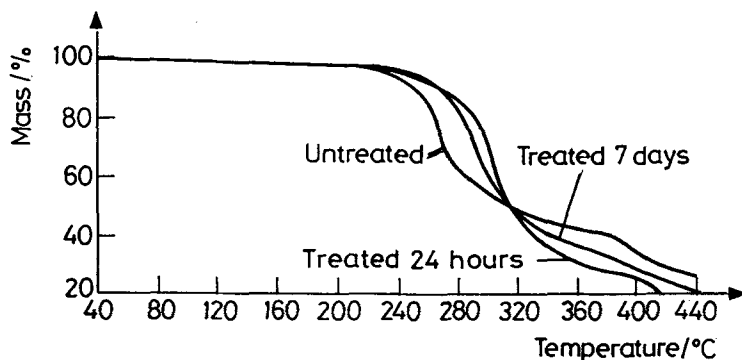


Fig. 1 Mass-loss vs. temperature for sample C-1 heated in nitrogen at  $2 \text{ deg}\cdot\text{min}^{-1}$

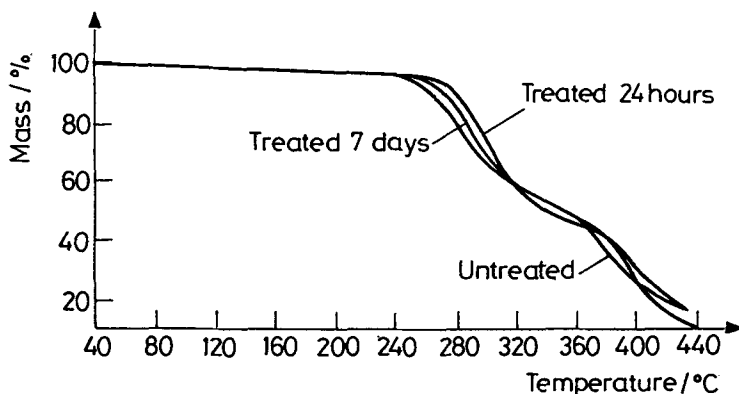


Fig. 2 Mass-loss vs. temperature for sample C-3 heated in nitrogen at  $2 \text{ deg}\cdot\text{min}^{-1}$

The reason for this improvement in stability is not apparent. The polyurethane should be quite fluid at these high temperatures and loses its diisocyanate, in one way or another, quite rapidly. At  $150^\circ\text{C}$  and in the presence of acid catalyst, methoxylated amide groups react with other amide groups by eliminating methanol and forming methylene bridges [11]. Grassie [7] has discussed

**Table 1** Temperatures at fixed percent mass-losses for methoxymethylated MDI-20% polymer (2000)-1,4 butanediol polymer (in nitrogen at 2 deg·min<sup>-1</sup>)

Time of methoxy- methylation treatment	Temperature (°C) at mass-loss of			
	5%	10%	15%	20%
a) (20% soft segment)				
(untreated)	234	252	260	267
24 hours	245	272	285	292
7 days	256	268	279	286
b) (50% soft segment)				
(untreated)	251	267	274	281
24 hours	270	282	291	297
7 days	259	274	281	288

mechanisms for thermal degradation of polyurethanes in considerable detail and finds that, at 250°C, a strong IR adsorption in the urea amide I region develops, thus indicating the formation of methylene links. However, the formation of these stable methylene links is not, in itself, a sufficient cause to account for the enhanced stability of the methoxymethylated polymer since the methoxymethylation occurs only in the surface layers, and this would not bring about improvement of stability in the bulk of the polymer.

#### *Initial mass-loss and very slow heating rate experiments*

The mass-losses upon heating a wide range of MDI and TDI - polyether and polyester soft segment - 1,4 butadiene polyurethanes have been investigated and the initial kinetic parameters determined [8, 13–15]. The mass-loss of several of these polymers has also been investigated over a 1000 fold heating rate range from 6 deg·min<sup>-1</sup> to 9 deg/day. We discuss here some of these results which especially illustrate the importance of the outward diffusion of products to kinetics of the degradation process.

The useful properties of a polymeric material often have deteriorated long before the time that the loss of material has become appreciable. Fortunately modern electrobalances are capable of measuring the first few percentages of mass-loss with high precision. The energy of activation,  $E$ , can be determined unambiguously at constant heating rate for low degrees of conversion from the slope of a plot of  $T^2[d\alpha/dT]$  vs.  $\alpha$  (or  $[d\alpha/d(1/T)]$  vs.  $\alpha$ ), from the equation [13, 14, 16]

$$\text{slope} = [d/dT][T^2(d\alpha/dT)] = E/R + 2T^* \quad (\alpha < 0.05) \quad (2)$$

where  $\alpha$  is the degree of, or fractional, mass-loss and  $T^*$  is the average temperature for the measurement range. A typical plot, here for a MDI-polyether soft segment-1,4 butanediol, is shown in Fig. 3. The near linearity of the slope of the plot to greater than five percent mass-loss before it begins to decrease indicates that the kinetics may be represented in this region by an  $n$ th order rate equation where  $n$  is only slightly greater than zero. Activation energies and temperatures at which 2, 4 and 6% mass-loss were reached are given for three MDI and three TDI polyurethanes in Table 2.

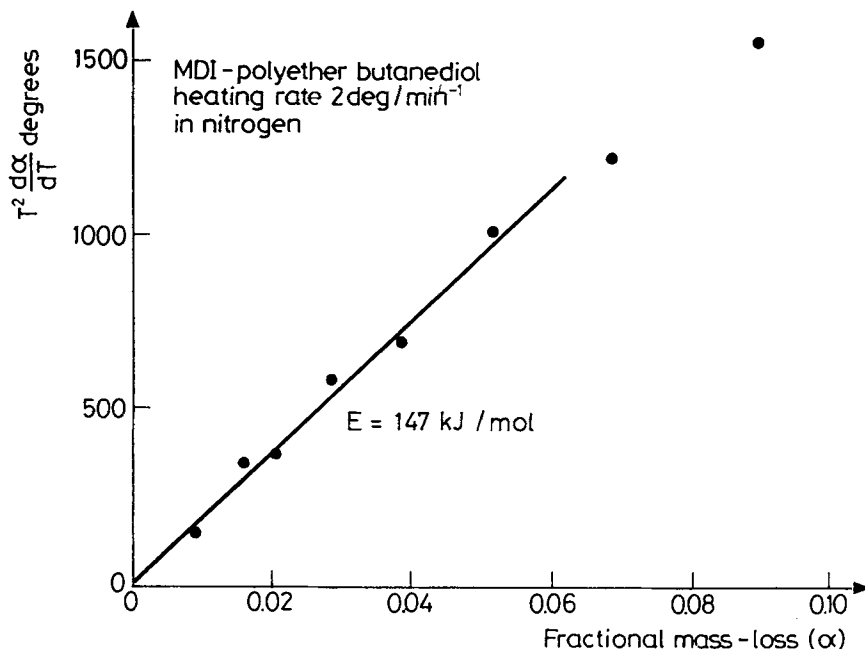


Fig. 3  $T^2 d\alpha/dT$  vs.  $\alpha$  for a MDI-polyether-butanediol in nitrogen at  $2 \text{ deg}\cdot\text{min}^{-1}$  heating rate

We have found, in general, that the TDI polyurethanes begin to lose mass at a temperature about 25 degrees lower than similar MDI polymers, and the TDI activation energies are about 20 kJ/mol lower. The diisocyanate is the smallest of the comonomers in polyurethanes and is the first product to be given off upon thermal treatment. Since MDI has a higher molecular mass than TDI, it appears that the greater stability of the MDI polymer at these accelerated conditions can be attributed to its slower rate of diffusion from the substrate. This hypothesis is further substantiated by the fact that hexamethylenediisocyanate

polyurethanes are more stable polyurethanes than MDI polyurethanes [17]. It has been found that molecules containing aromatic rings diffuse much more rapidly through polyolefin matrices than do aliphatic migrants of comparable molecular mass [18]. Therefore this is supporting evidence that the rate controlling step of the degradation reaction is the diffusion of the diisocyanate moiety from the polyurethane matrix.

**Table 2** Early activation energies and temperatures at fixed percent mass-loss for several polyurethanes (in nitrogen at 2 deg·min<sup>-1</sup>)

Polyurethane (—)	<i>E</i> /kJ·mol <sup>-1</sup>	Temperature (°C) at mass-loss of		
		2%	4%	6%
(1,4 butanediol)				
TDI polyester	117	220	230	237
TDI polymeg 1000	125	235	247	254
TDI polymeg 2000	130	239	252	261
MDI polyester	150	269	281	288
MDI polymeg 1000	155	262	271	278
MDI polymeg 2000	147	260	263	268

**Table 3** Early activation energies and temperatures at fixed percent mass-losses for a MDI-polymeg 2000-1,4 butanediol in various nitrogen-oxygen mixtures (flow rate, 200 ml/min; heating rate, 2 deg·min<sup>-1</sup>)

% Nitrogen/ % Oxygen	<i>E</i> (1-4%)/kJ·mol <sup>-1</sup>	Temperature (°C) at mass-loss of		
		2%	4%	6%
100/ 0	138	250	262	268
99/ 1	125	271	278	282
90/10	130	265	278	282
80/20	88	233	250	269
50/50	84→42	200	218	240

The effect of various ratios of nitrogen/oxygen in the purge gas, for a MDI-Polymeg 2000-1,4 butanediol polyurethane, upon the early activation energy and the temperatures to reach mass-losses of 2, 4 and 6% are given in Table 3. The activation energies for the 1-4% mass-loss range do not change appreciably until the oxygen concentration reaches that of air (20%) whence it falls from about 135 to 88 kJ/mol. This latter value for the activation energy is typical for the oxidative degradation of many polymers in air. At 50% oxygen, the



initial kinetics become erratic, and the apparent activation energy, calculated from Eq. (2), varies from 84 to 42 kJ/mol.

The most striking effect of oxygen upon the mass-loss kinetics is that higher temperatures are necessary to obtain 2, 4 and 6% conversion in 1 and 10% oxygen atmospheres than were needed to obtain the same degrees of conversion in pure nitrogen. It appears, as was the case for the methoxymethylated polyurethanes, that this slowing of the degradation process is again a result of hindered diffusion caused by the incorporation of these bulky oxygen-containing groups into the polymer, especially at its surface. Evidence for the occurrence of such an oxidation reaction at even lower temperatures will be given subsequently. On the other hand, the degradation temperatures in 20/80 and 50/50% oxygen/nitrogen mixtures are lower than in pure nitrogen. This behaviour is typical of many polymeric systems since the oxidative reaction becomes autocatalytic at higher oxygen concentrations.

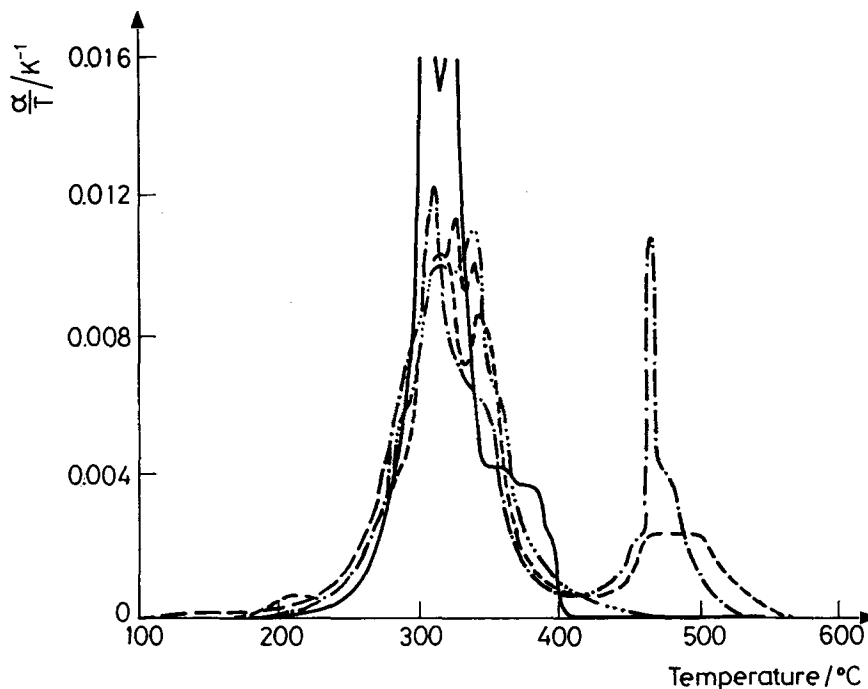


Fig. 4  $d\alpha/dT$  vs. temperature for a MDI-polyester-butanediol at  $6 \text{ deg min}^{-1}$ . Purge gas compositions are: — vacuum, ···· nitrogen, --- nitrogen, water vapor, - - - - air, - · - · - air, water vapor

Further evidence in regard to the effects of diffusion of product species upon the mass-loss kinetics can be obtained from the comparison of the derivative

curves under different purge gas atmospheres. The rate of mass-loss with respect to temperature, at a heating rate of  $6 \text{ deg}\cdot\text{min}^{-1}$ , is plotted against temperature in Fig. 4 for experiments in vacuum, in air, both with and without water vapor, and in nitrogen, both with and without water vapor, for a polyester soft segment MDI-1,4 butanediol polyurethane. At the beginning of the reaction, the mass-loss occurs at a slightly slower rate in vacuum than in nitrogen at atmospheric pressure. However, these curves for the various purge atmospheres in the first portion of the mass-loss are relatively unaffected by changes in the composition of the purge gas. This lack of dependence on purge gas pressure is quite unusual. For most polymers, the mass-loss in vacuum occurs at temperatures as much as fifty degrees below temperatures for onset of mass-loss in nitrogen. Thus, for these polyurethanes, even under high vacuum, the escape of the diisocyanate moiety is not enhanced. Grassie and Mendoza [19] have noted a reversal of rates for a polyether soft segment polyurethane where the rate of mass-loss in nitrogen is more rapid than the rate under vacuum in the initial stages. This surprising event has never been satisfactorily explained. The above results further substantiate the hypothesis that hindered diffusion prevents the diisocyanate from escaping until its diffusion coefficient increases, either as a result of a phase change or of the softening of the polyurethane. When air is the purge atmosphere (Fig. 4), a char is formed which burns off at about  $450^\circ\text{C}$ .

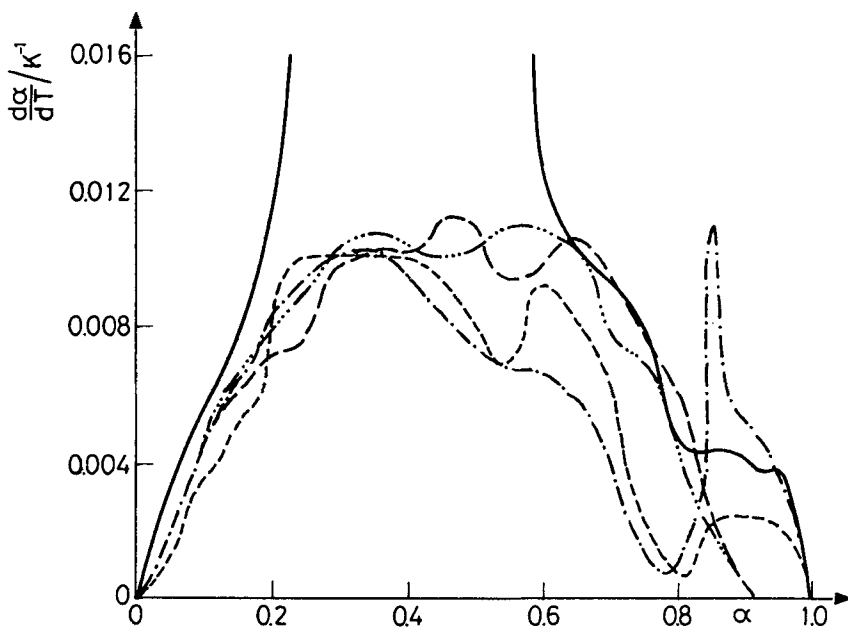


Fig. 5  $d\alpha/dT$  vs.  $\alpha$  for a MDI-polyester-butenediol at  $6 \text{ deg}\cdot\text{min}^{-1}$ . (See legend of Fig. 4 for the composition of purge gases.)

The differences between the mass-loss curves for the various atmospheres can be seen more clearly in Fig. 5 in which rate vs. conversion (rather than temperature) is plotted for the same data as in Fig. 4. The reaction, once begun, does accelerate more rapidly in vacuum and 40% mass-loss occurs almost explosively at 300°C. The reaction reaches 100% conversion by 450°C.

The explosive loss of mass between 0.2 and 0.6 degrees of conversion, seen in Fig. 5, also occurred when many of the other MDI and TDI polyurethanes were heated at 6 deg·min<sup>-1</sup> in vacuum. This is further evidence for the build up of an internal pressure of the diisocyanate moiety within the bulk of the polymer. These 'bursts' have been noted during the decomposition of other polymers. Stoch [20] has developed a 'Sealed Box' model for this phenomenon when it occurs during the dehydration of inorganic solids.

Water vapor has no effect upon the rate during the nitrogen purge experiments, which result in a 10% residue. Water vapor suppresses the reaction at 60% mass-loss but catalyses the burning of the carbonaceous residue in the 500–600°C range. Otherwise, water vapor has little effect on the kinetics at these relatively fast heating rates and high temperatures.

Slowing the heating rate a thousand fold to 9 deg/day (Fig. 6) for the same polyester soft segment polymer shifts the degradation reactions down to the 150–300°C temperature range and better separates the component reactions. For example, the suppression of the rate of mass-loss by air in the 175 to 250°C range is clearly evident. In the presence of dry oxygen, a weight gain (formation of hydroperoxy groups?) occurs around 130–145°C. The sudden equivalent mass-loss at 150°C is a chemical reaction involving oxygen-containing groups. The presence of water vapor in the oxygen purge completely suppresses the above mentioned mass gain and loss at low temperatures. The char-burning reaction temperature in air is decreased to the 300°C range at this extremely slow heating rate. There is evidence of a peak in the intermediate temperature ranges which probably is a result of the hydrolysis of the ester groups.

These experiments at very slow heating rates produce more interpretable data, especially for the initial phases of the degradation reaction. If the polymeric material has been well characterized beforehand, then the initial part of the reaction will be amenable to interpretation of mechanism of its kinetics. Later on in the reaction, the physical state and chemical composition of the substrate have been altered in unknown and complex ways. It is the kinetics parameters obtained from the earliest mass-loss measurements which give the greatest promise of being useful in the prediction of service lifetimes.

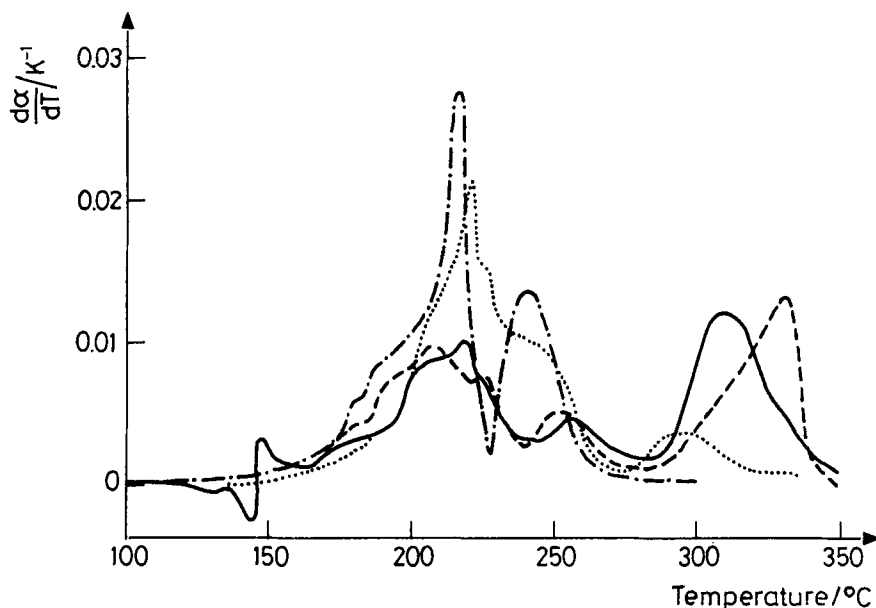


Fig. 6  $d\alpha/dT$  vs. temperature for a MDI-polyester-butanediol at 9 deg/day. Purge gas composition are:— air, --- air, water vapor, ··· nitrogen, — · — · — nitrogen, water vapor

## Conclusions

Evidence has been presented that it may be practical to extend the service life of polyurethanes by chemical treatment which incorporates bulky additions in their surface layers, thereby hindering the diffusion of depolycondensed diisocyanate from the interior and suppressing the depolycondensation reaction.

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**Zusammenfassung** — Wie durch TG nachgewiesen wurde, resultieren sowohl Oxidation als auch Methoxymethylierung der Oberfläche einer Serie von 1-4 Butandiolpolyurethanen mit MDI- (Methylendiphenylisocyanat) und TDI- (Toluoldiisocyanat) Polyether- und Polyester-softsegmenten in einer gesteigerten thermischen Stabilität. Die explosionsartige Massenabgabe oberhalb der Hardsegment-Schmelztemperatur deutet darauf hin, daß die Diffusion der dissoziierten Diisocyanatkomponente bei niedrigeren Temperaturen behindert ist. Somit kann die Unterdrückung der Depolykondensationsreaktion durch chemisches Blockieren der Oberfläche in einem Material mit erhöhter Standzeit bei Gebrauchstemperaturen resultieren, da die thermische Stabilität eines Polyurethanes von der geringen Diffusivität seines Diisocyanat-Komonomeres abhängen kann. Weiterhin wird der Einfluß von Vakuum, Sauerstoff und Wasserdampf auf die Kinetik der Massenabgabe einiger Polyurethane dargestellt.