Thermal Degradation of Segmented Polyurethanes

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SYNOPSIS

Thermal degradation of polyurethane samples was studied by a thermogravimetric method. The effect of soft-segment length and soft-segment concentration on activation energy of the degradation process was measured. Three methods of calculation gave activation energies at different stages of the very complex weight loss process. It was shown that at initial stages of the weight loss the process was dominated by hard-segment degradation. Activation energy of the whole process calculated by the Ozawa–Flynn method did not offer clear insight into the structure–stability relationship of polyurethanes. The second method showed that activation energy of the initial stage of degradation increased with decrease in hard-segment length. The Flynn method of calculating activation energy produced fairly constant activation energy of the first 40% degradation, at around 150 kJ/mol, for polymers in the C series. Generally, calculation of kinetic parameters of a complex degradation process as in polyurethanes gives results that are not easy to interpret. It has been shown qualitatively that polymers with higher soft-segment concentration display lower initial weight loss and higher onset temperatures of degradation. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Thermal stability of polyurethanes was studied extensively because of the great importance of this group of materials.[1–10] Generally speaking, polyurethanes are not very thermally stable polymers. The onset degradation temperature of the urethane bond depends on the type of isocyanate and alcohol used. It is a general rule that the more easily formed urethanes are less stable, i.e., more easily dissociated than are the more difficulty formed ones. Thus, the highest degradation temperature, about 250°C, is observed[11] for a urethane formed from alkyl isocyanate and alkyl alcohol, followed by an aryl isocyanate–alkyl alcohol combination (degrading at about 200°C), an alkyl isocyanate and aryl alcohol (stable up to 180°C), and an aryl–aryl combination whose temperature limit is in the 120°C range. These temperatures are approximate since they depend on the rate of heating or time of exposure to isothermal conditions. It is important to stress that the results of thermal stability measurements are strongly dependent on the method of measurement. Our study of thermal stability of polyurethanes showed that the order of stabilities measured by weight loss of a series of segmented polyurethanes was the opposite of that obtained by mechanical measurements after exposure to high temperatures, where a decrease in strength was used as the stability criterion.[12]

Polyurethanes are a broad class of polymers that may have very different structures and have in common only the presence of a urethane group, which often is less frequently occurring than some other groups, as in the case of segmented polyurethanes. In such complex systems, thermal stability is governed not necessarily by the weakest link in the chain but often by the most frequently occurring one and by the environment of the given groups. It has been shown that the polyether soft segment and the MDI/piperazine hard segment are more stable when mixed in the copolymer than when in separate phases.[13]

To explain such behavior, it is instructive to analyze degradation of each component (segment) separately. Poly(tetramethylene oxide) (PTMO) degrades easily in air by oxidation at the β-carbon

next to the ether bond. Breakage of the C — O bond and subsequent unzipping was proposed as the mechanism in an inert atmosphere.[14] Polyurethane is thermally degraded through three basic mechanisms: the urethane bond dissociating into its starting components, i.e., alcohol and isocyanate; breaking of the urethane bond with formation of primary amine, carbon dioxide, and an olefin; and, finally, splitting the urethane bond into secondary amine and carbon dioxide.[15]

Transurethanization, a process analogous to transesterification in polyesters, has been observed. When both segments are present, then amines from the hard segment may act as traps for radicals formed in the soft segment, thus affecting the thermal stability of the soft segment. The thermal stability of more complex systems, such as segmented polyurethanes, depends both on segment lengths and their concentration, which are related to the sample morphology.

In this work, we studied the kinetics of thermal degradation of a series of segmented polyetherurethanes based on diphenylmethane (MDI) and polytetramethylene (PTMO) glycols of various molecular weights with butane diol as the chain extender. Soft-segment molecular weights were 650 (series A), 1000 (series B), and 2000 (series C). Soft-segment concentration (SSC) in each series was varied from zero to maximum values from 68% to 80%, depending on the series. A general discussion of structure–property relationships in segmented polyurethanes is given in the review article in Ref. 16.

EXPERIMENTAL

Materials

Three series of polyurethanes were synthesized by a prepolymer technique. Synthesis and properties of these polyurethanes was described previously.[17,18] Polymers were purified by dissolution in dimethylformamide and subsequent precipitation from water to remove low molecular weight species. Polymers were redissolved in DMF and cast in films, which were used for mechanical and thermal tests. Designation of samples is given in Table I.

Methods

The kinetics of degradation of segmented polyurethanes was measured using a DuPont 1090 Thermal Analyzer with TGA module 910. Heating rates of 0.5°/min, 1°/min, and 2°/min were used. The ni-

Table I   Designation of Polyurethanes

Series A (soft segment MW = 650)

SSC (%)	20	40	50	60	68
Sample designation	A1	A2	A3	A4	A5

Series B (soft segment MW = 1000)

SSC (%)	20	40	50	60	77.5
Sample designation	B1	B2	B3	B4	B5

Series C (soft segment MW = 2000)

SSC (%)	20	40	50	60	80	87
Sample designation	C1	C2	C3	C4	C5	C6

Sample ABC, pure hard segment (SSC = 0%), was common to all series.

trogen flow rate was kept at 50 mL/min. The sample weight was about 10 mg. Since some methods of kinetic analysis require measurements of isothermal weight loss, this test was carried out at 270°C, but only on the C-series samples.

RESULTS AND DISCUSSION

Determination of meaningful kinetic parameters of the degradation process from TGA curves is a not a simple task. For example, Nishizaki et al.[19] applied several methods of calculation to measure kinetic parameters of polystyrene degradation from TGA data. The results were strongly dependent on the method of calculation applied. The same group of integral and differential methods was tested on the synthetic TGA curve, but the results showed that all methods applied were correct providing that one is dealing with the simple reaction mechanism, characterized by a single reaction order and single activation energy, which for polymers is seldom the case.[20] Thus, the reaction order of the system of complex reactions as in degradation of polymers is not necessarily a meaningful parameter. The activation energy of the process can seldom be assessed correctly from a single TGA curve. More reliable methods involve several dynamic and isothermal curves. The slower the heating rate, the better the resolution of the degradation processes will be. A typical weight loss curve (TGA) and differential weight loss (DTGA) curve are shown in Figure 1.

The TGA curve displays two distinct regions of weight loss that are reflected in two peaks in the
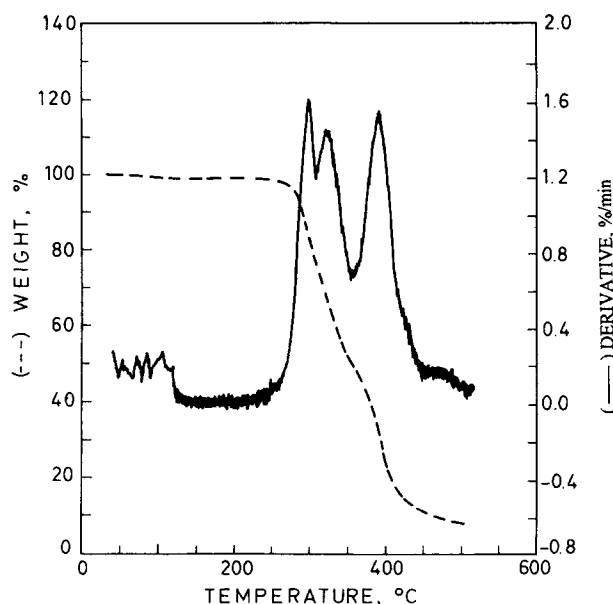
Figure 1 TGA and DTGA curves of sample B3 at the heating rate of 2°/min.

DTGA curve. Sometimes, as shown in Figure 1, the first part of the degradation is split into two peaks, illustrating the complexity of the process. The size of the second peak of the first part was found to correlate with the soft-segment concentration. It was established previously that the amount of weight loss is well correlated with the hard-segment concentration, suggesting that degradation starts in the hard segment.[21] Qualitative characterization of the

degradation process is illustrated by the onset and maximum temperatures of the first step, T_{1on} and T_{1max}, the same for the second step, T_{2on} and T_{2max}, and temperature of the peak between these two, T_{12max}, if it exists. The process ends with the loss of all volatile material and with char residue that does not change much above 500°C. Table II presents the characteristic temperatures of degradation at 1°C/min heating rate.

Table II shows that the onset temperature of the first step increases with the increase of the SSC, whereas the onset temperature of the second step decreases with the increase of the SSC. There was no significant effect of the soft-segment length on the characteristic temperatures. However, the amount of weight loss in the first step was higher in the series with shorter soft segments. It decreased with the increase in SSC, as shown in Figure 2.

Since weight loss in the first stage is governed mainly by the degradation of the hard segments, it appears that longer hard segments were degraded in a different way than were the shorter ones. Weight loss in the second step increased with the increase of SSC and segment length. The effect of soft-segment length on degradation is illustrated in Figure 3. Samples A4, B4, and C4 have 60% SSC but different soft- and hard-segment lengths. Differences in stability appear at the middle stage of degradation, with longer soft segments giving higher stability.

The morphology of these samples below melting is characterized by a continuous soft phase with dispersed hard domains in it. The effect of soft-segment

Table II Characteristic Points on TGA Curves at 1°C/min

| Sample	T_{1on} (°C)	T_{1max} (°C)	T_{12max} (°C)	T_{2on} (°C)	T_{2max} (°C)	Residue at 450°C (%)
ABC	100	230	305	260	340	48
A1	240	275	320	370	415	25
A2	250	295	317	360	400	15
A3	250	295	317	355	392	10
A4	255	290	310	340	385	5
A5	258	—	317	350	380	9
B1	220	290	345	370	420	22
B2	220	290	320	355	395	19
B3	245	287	310	347	385	15
B4	250	—	325	350	385	10
B5	280	—	338	360	385	10
C1	240	295	325(?)	370	410	22
C2	245	280	340	370	400	17
C3	256	294	316	346	382	9
C4	240	295	320	345	385	12
C6	280	—	325	340	370	3
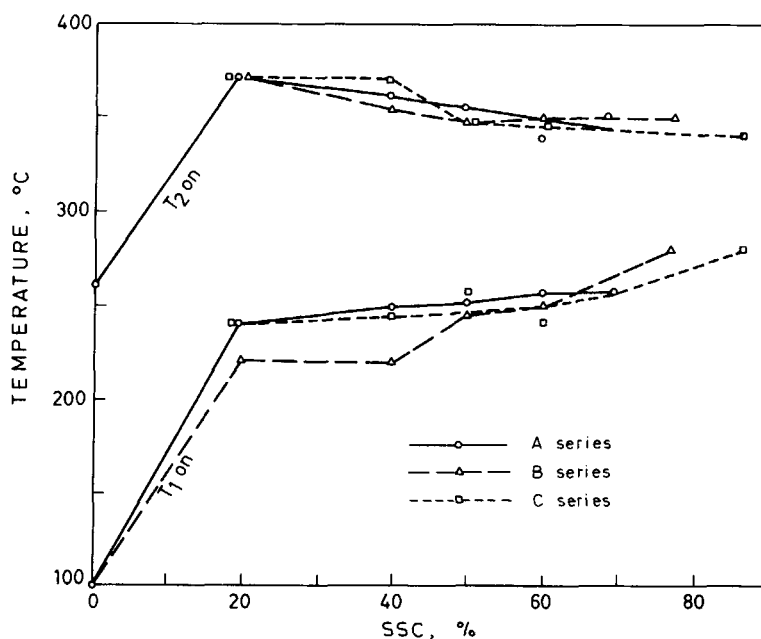
Figure 2   The effect of SSC on characteristic degradation temperatures.

concentration is illustrated in Figure 4 where three samples in C series, having 20%, 50%, and 87% SSC, are compared. Figure 4 clearly shows that samples with higher SSC have higher stability at the initial stages. Here, sample C1 is characterized by continuous hard phase with a dispersed soft phase in it, whereas sample C3 has both continuous phases and lamellar morphology and C6 is essentially a one (soft)-phase system. Above the melting point of the hard segment, which is at about 180°C, this morphology is destroyed.

The picture presented in Figures 1–4 shows that at least two stages of degradation occur. Kinetics of

the degradation process was characterized by measuring activation energy, which was calculated from experimental data using three methods. Since the mechanism of degradation of these complex systems changes during degradation, activation energy is not only a function of chemical structure of polymers but also changes with conversion for a single polymer. It provides, however, among other things, an additional parameter for the assessment of the thermal stability of these polymers.

The first method of calculation of activation energy, proposed by Ozawa and Flynn,[22,23] requires several TGA curves at different heating rates. It
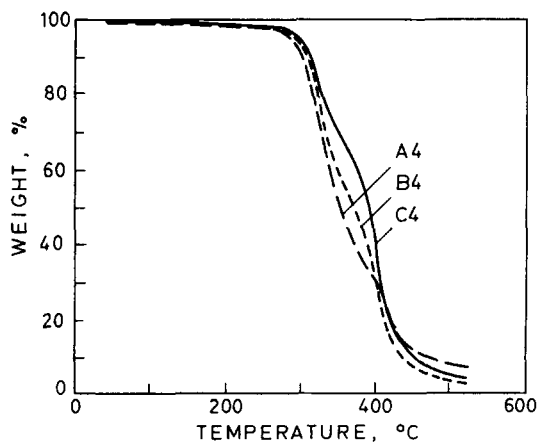

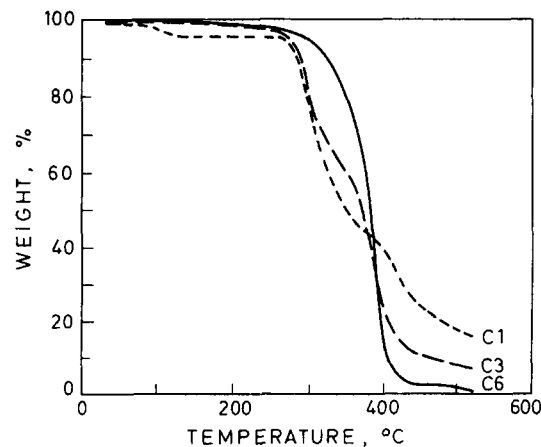**Figure 3**   TGA curves of samples A4, B4, and C4 obtained at 2°C/min.

Figure 4   TGA curves of samples C1, C3, and C6 obtained at 2°/min.

consists of plotting the logarithm of heating rate ($\log_{10}\beta$) vs. $1/T$ for each degree of conversion (α), defined as the weight loss at a given temperature divided by total weight loss. Usually, α was taken to be 0.1; 0.2; $\cdot$ $\cdot$ $\cdot$ 0.9. From these isoconversion curves, activation energy (E_a) was calculated for each conversion and the average value for the whole range of conversions. Sometimes, the crossing of TGA curves at different heating rates was observed. In this case, no E_a could be calculated. Activation energy was calculated from the slope of the lines using the expression

$$E_a = \frac{\text{slope} \times R}{0.457}. \tag{1}$$

where R is the gas constant. The application of this method on samples A2 and A3 is illustrated in Figure 5. Figure 5 shows straight lines with fairly good correlation coefficients, which is not always the case.

To cross-check the results, a second method of calculation was used.[24,25] This method is applied only to low conversions, between 1 and 9%. According to this method, a diagram $T^2(d\alpha/dT)$ vs. α is constructed. Activation energy is obtained from the slope of the straight lines using the following relationship:

$$E_a = (R \times \text{slope}) - 2RT. \tag{2}$$

The application of this method is illustrated in Figure 6. Figure 6 shows good correlation between two variables and adequate straight lines that allow reliable calculation of kinetic parameters at low percent weight-loss.

The third method proposed by Flynn[26] requires three dynamic TGA curves obtained at different heating rates and one isothermal curve. Here, a logarithm (ln) of time to reach certain conversion is plotted vs. reciprocal temperature at which the same conversion is obtained for a given heating rate. Activation energy is obtained from the slope of straight lines at each heating rate, using the relationship

$$E_a \approx \text{slope}/1.05. \tag{3}$$

This method was applied only to C series samples. An illustration of the application of the Flynn method is given in Figure 7(a) and (b).

The activation energy measured by all three methods are given in Tables III–V. The results calculated by this method show broad variation of E_a with the degree of conversion, which is expected, due to the constant change of degradation mechanism. In the "A" series, E_a generally increases, but not regularly, with the increase in conversion. However, no clear trend was observed with B and C series polymers, and activation energies were clustered about 150 kJ/mol. Since the samples undergo great changes at high conversion, the values of E_a above 50% weight loss are not meaningful. In some cases, only those values could be calculated. Thus, it is difficult to reach a definite conclusion on the effects of SSC and soft-segment length on activation energy. The trend of change of average activation energy with SSC or segment length is not clear.

Activation energies of the samples in all three series, calculated by the second method, are given in Table IV. The average values of these "initial" activation energies in the A series is 184 kJ/mol; in
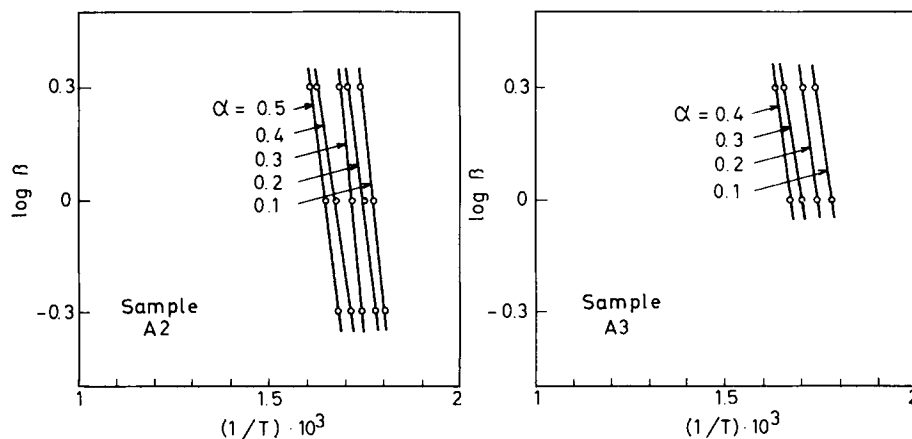

Figure 5 The dependence of $\log_{10} \beta$ on $1/T$ for samples (a) A2 and (b) A3, necessary for the application of Ozawa–Flynn method.
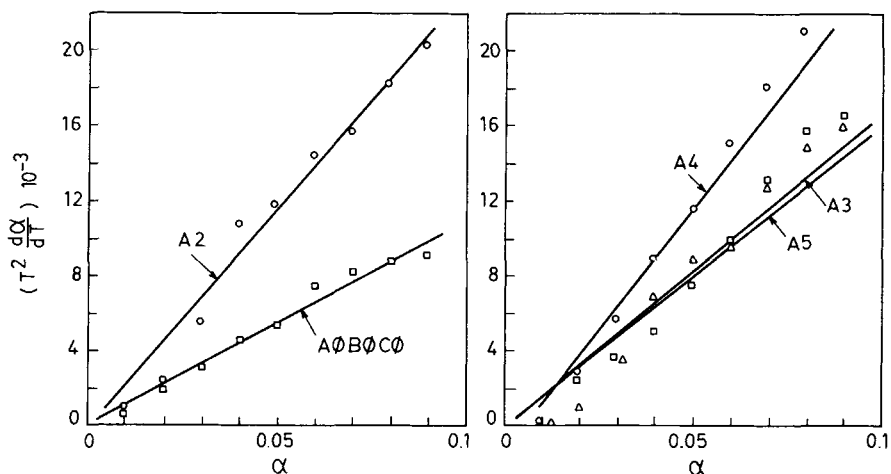
Figure 6   Dependence of $T^2(d\alpha/dT)$ on the degree of conversion, α, for samples (a) ABC and A2 and (b) A3, A4, and A5.

the B series, 154 kJ/mol; and in the C series polyurethanes, 135 kJ/mol. It should be emphasized that hard segments in polymers in the A series are shorter than those in the B series, whereas those in the C series are the longest, for the same soft-segment concentration. Because method 2 reflects kinetics of the initial phase of degradation dominated by degradation of the hard segments, higher average activation energies for the A series obtained by method 2 suggest that shorter hard segments are initially more stable than are the longer ones. Since polymers with lower SSC in each series also have longer hard segments, it would be expected that activation energy increases with the increase of SSC, which is not confirmed beyond doubt. It may be that the difference in segment lengths is not great enough to show clear differences, since all values are in the region of oligomers. Figure 8 displays the change of

activation energy with SSC for three series of polyurethanes. Although there is considerable scatter, the values are clustered about 150 kJ/mol.

The application of the third method to calculate activation energies on the C series polyurethanes produced a new set of results, shown in Table V. Here, the activation energy was measured at four conversions, 0.1, 0.2, 0.3, and 0.4, and heating rates at 0.5°/min, 1°/min, and 2°/min. Calculated results were found to depend on the heating rate, so the average of three values, E_{av}, are also given in Table V.

The values reported in Table V reflect kinetic properties in a broader range of conversions than by method 2. Sample C6 is not a segmented polymer but a one-phase system consisting of the polyol and MDI only. Sample C4 displayed unusually low activation energies, which could not be explained by
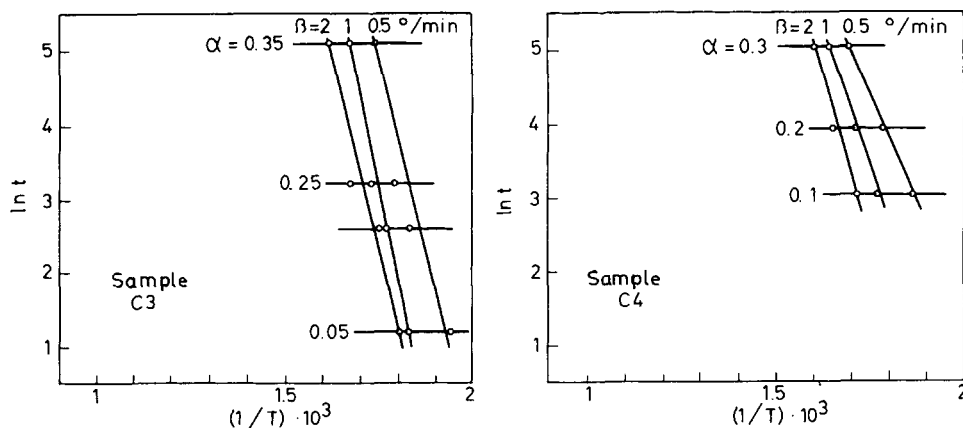

Figure 7   Dependence of ln t on $1/T$ for polymers (a) C3 and (b) C4.

Table III Activation Energies in kJ/mol of the Polyurethane Degradation Process Calculated by Ozawa–Flynn Method

| Sample | Conversion | | | | | | | | |
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	E_{av}
ABC	14	79	89	118					95
A1	121	90	122	164	159	180			139
A2	168	147	176	121	148	158	119		152
A3	177	183	130	130	391				155
A4	165	184	176	171	171	216			179
A5	226	296							261
B1	411	470	444						449
B2	50	107	160						139
B3	233	183	171	152	208				189
B4	104	112	134	129	180				132
B5				106	108	109	115	110	110
C1	128	126	86	91					106
C2	119								119
C3	90	123	86	76					93
C4	78	99	119	164	168	199	240		152
C5	327	224							275
C6	108	114	124	132	146	132	132	162	131

structural parameters and which are probably the consequence of experimental problems. Samples C2, C3, and C5 have about the same activation energies, suggesting that there is no significant effect of SSC

Table IV Activation Energies of Polyurethane Degradation Process Calculated by the Second Method

Polymer	Temperature (K)	E_a (kJ/mol)
ABC	469	84
A1	—	—
A2	538	200
A3	561	164
A4	544	211
A5	554	211
B1	511	63
B2	523	127
B3	530	250
B4	538	131
B5	581	138
C1	502	138
C2	543	165
C3	482	62
C4	519	215
C5	562	116
C6	576	117

on the first step of degradation process. However, an unusually high E_a of the C1 polyurethane is not in line with the results of two other methods, although it measures somewhat different properties. Figure 9 shows TGA curves of samples C1, C2, C3, and C4 obtained at 2°/min. This figure illustrates a qualitatively higher thermal stability of C4 and not a superior thermal stability of C1 compared with the other three polymers. The higher E_a for C1 from Table V probably is the result of other factors.

CONCLUSIONS

It has been shown that thermal degradation of segmented polyurethanes is a very complex process.

Table V Activation Energies of the Degradation Process Calculated by the Flynn Method

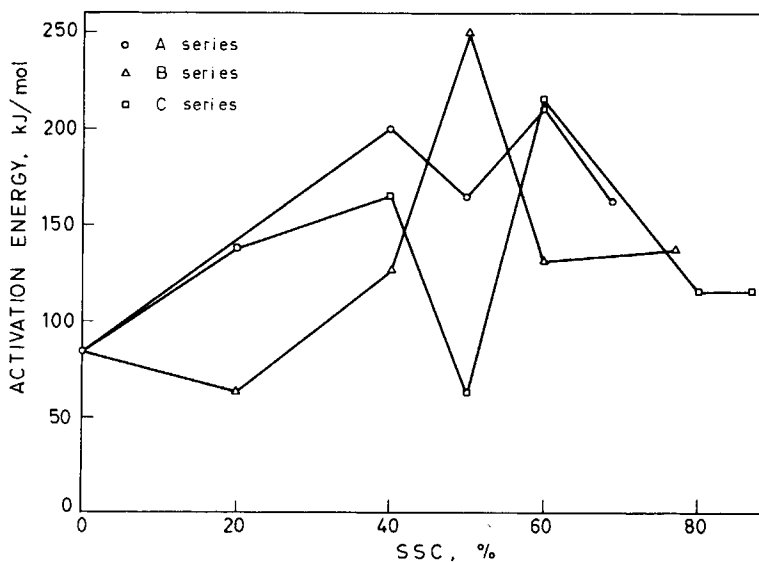| Sample | Heating Rate (deg/min) | | | |
	0.5	1	2	E_{av}
C1	185	164	201	184
C2	147	147	147	147
C3	147	210	157	152
C4	93	131	139	121
C5	144	230	161	152
C6	170	—	82	126

Figure 8   Change of activation energy, calculated by method 2, with SSC, for three series of polyurethanes.

The effect of soft-segment length and soft-segment concentration on the apparent activation energy of the degradation process was measured and three methods of calculation applied. All methods gave different apparent activation energies, as expected, since they were applied to different stages of degradation. The Flynn method of calculating activation energy produced fairly constant activation energy of the first 40% degradation, at around 150 kJ/mol, for polymers in the C series. Generally, calculation of kinetic parameters of complex degradation process as in polyurethanes does give results that are not easy to interpret. A qualitative picture
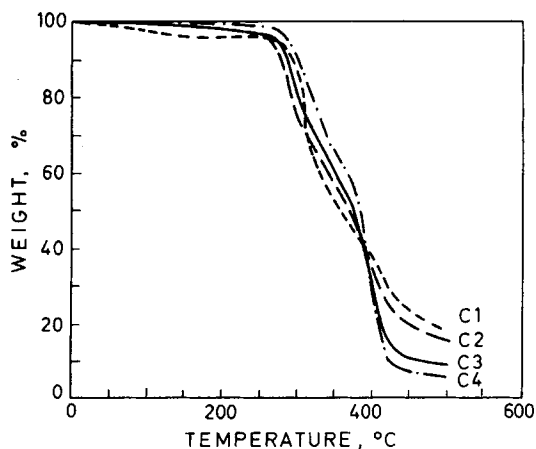
of the stability of segmented polyurethanes was obtained by comparing weight loss at different stages.

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Figure 9   TGA curves of samples C1, C2, C3, and C4 obtained at the heating rate of 2°/min.

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