STRUCTURAL INFORMATION FROM DEGRADATION STUDIES

Norman Grassie

Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland

Abstract - Small structural differences in a series of closely related polymers may have a profound effect on the nature of their degradation reactions. Neither may it be assumed that the degradation behaviour of copolymers may be inferred from the behaviours of the homopolymers of the constituent monomers. Even the experimental conditions, the physical state of the polymer and the presence of impurities may have a profound effect upon the course of the degradation process. These generalisations are illustrated by reference to the polymethacrylates and polyacrylates, the methyl and phenyl substituted polysiloxanes and polyurethane.

### INTRODUCTION

The identification of the products of decomposition of complex organic molecules under carefully controlled conditions has always been a useful technique for assisting in the determination of their structure. This kind of approach has also been important in the field of synthetic polymers although its application has been rather in the direction of understanding how these materials break down under the influence of the various environmental conditions to which they may be exposed in use. In this way it may be more easily understood how their commercial applications may be extended by a better understanding of how optimum stability may be achieved either by attention to molecular structure or by the use of additives which may increase their stability towards, for example, heat, light or oxidation.

The results of the large volume of degradation work which has been carried out throughout the world during the past 30 years have clearly been of great value in this way to the commercial polymer producer. It would be quite impossible in this paper to review all the work which has been done. Instead, I intend to take a narrower view and to demonstrate, by reference to examples with which I am familiar, some of the effects which quite small differences in chemical structure may have on polymer stability and how one may be led to erroneous deductions by over zealous generalisation. For example, it must not be assumed that series of structurally very similar materials will have similar degradation properties. Neither may it be assumed that the degradation behaviour of copolymers will be the average of the behaviours of the homopolymers of the constituent monomers. Similarly the conditions under which the degradation is carried out, the physical state of the polymer and the presence of additives or impurities may all affect the course of the degradation process.

### POLYMETHACRYLATES AND POLYACRYLATES

The large differences which may be observed in the degradation characteristics of a series of structurally similar polymers is demonstrated by the series of polymethacrylates.

In the thermal degradation of poly(methyl methacrylate) (PMMA), radicals are formed by scission of main chain bonds. The radicals then unzip, or depropagate, to give very high yields of monomer.

With higher methacrylate esters, ester decomposition reactions become possible resulting in methacrylic acid units in the polymer and formation of the corresponding olefin. The most thoroughly studied system of this kind is poly(t-butyl methacrylate) (Ref. 1). The reaction proceeds by a molecular mechanism involving interaction between the carbonyl group and hydrogen atoms on the  $\beta$  carbon atom of the ester group.

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The importance of  $\beta$  hydrogen atoms in facilitating ester decomposition at the expense of depolymerisation is illustrated by the data in Table 1 (Ref. 2).

TABLE 1. Mechanisms of thermal degradation of poly(alkyl methacrylates)

Depolymerisation		Mainly Depolymerisation		Ester Decomposition	
Methyl	0	Ethyl	3	iso-Propyl	6
neo-Pentyl	0	n-Propyl	2	sec-Butyl	5
iso-Butyl	1	n-Butyl	2	tert-Butyl	9
Ethoxyethyl	2	n-Hexyl	2		
		n-Heptyl	2		
		n-Octyl	2		

Thus ester decomposition only becomes important when the monomer unit incorporates five  $\beta$  hydrogen atoms and depolymerisation is quantitative when there are at most one or two  $\beta$  hydrogen atoms.

However the mode of initiation of degradation may also have a profound effect on this pattern of behaviour. It is found that if any of these methacrylate polymers is subjected to uv irradiation in the temperature region 100-200°C, that is below the thermal degradation temperature but above the softening point, then the monomers are always formed in 100% yield in complete absence of ester decomposition, even with poly(t-butyl methacrylate). This dramatic effect of uv irradiation is illustrated in Fig. 1 (Ref. 3). These

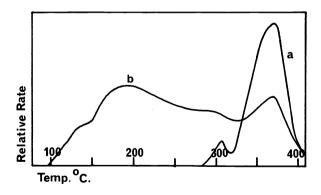


Fig. 1. TVA curves for PMMA. a, heat only; b, heated and simultaneously irradiated with 253.7 nm radiation. (heating rate,  $10^{\circ}$ C min<sup>-1</sup>).

Thermal Volatilisation Analysis (TVA) (Ref. 4) curves represent the rate of evolution of monomer from poly(methyl methacrylate) as it is heated dynamically at  $10^{\circ}$  min<sup>-1</sup>.

The next most obvious question to be asked is why monomer production does not occur below the softening point of the polymer which is in the vicinity of 100 °C. In fact, quite different behaviour is observed below this temperature under uv irradiation. Firstly, volatile products including methyl formate, carbon monoxide, carbon dioxide, methanol and methane are formed and secondly, there is a rapid decrease in molecular weight. These facts can be accounted for in terms of the following sequence of reactions.

But then we may ask, why is monomer not liberated by depropagation of the chain end polymer radical as at higher temperatures? The answer follows from the fact that propagation/depropagation is a reversible process.

in which  $P_{0}$  and  $P_{0}$  are polymer radicals n and n+l units in length and M is a monomer molecule. In polymerising monomer the high concentration of monomer drives the reaction to the left while in degrading molten polymer the monomer can freely escape as it is formed so that the reaction is driven to the right. Below the softening point, however, monomer can not readily escape so that the polymer radicals are effectively surrounded by monomer molecules and depropagation is inhibited.

This influence of the physical state, which is related to the glass transition temperature  $(T_g)$  is also demonstrated by the photodegradation behaviour of copolymers of methyl methacrylate and methyl acrylate. Unlike poly(methyl methacrylate), poly(methyl acrylate) becomes insoluble on uv irradiation. However the gaseous products, which are derived from scission of the ester groups, are the same. Thus the initially formed chain side radicals of polyacrylates combine to form cross links.

When films of copolymers covering the whole composition range are irradiated only those containing more than 50% methylmethacrylate remain soluble (Ref. 5). Copolymers containing more than 50% methyl acrylate become insoluble. Extents of chain scission and cross linking can easily be determined experimentally with the result shown in curves a and b in Fig. 2. It is perhaps to be expected that the rate of cross linking decreases with methyl acrylate content and that the rate of chain scission decreases as the methyl methacrylate content is decreased. But the minimum in the rate of chain scission in the vicinity of 40-50% methyl methacrylate and the subsequent rapid increase so that the rate of chain scission in pure poly(methyl acrylate) is of the same order as that in pure poly(methyl methacrylate) is perhaps surprising.

In solution, uv radiation does not cause insolubility in poly(methyl acrylate) as it does in film. This is because cross linking is inhibited in solution by separation of the polymer molecules by molecules of the solvent. Chain scission in copolymers in solution

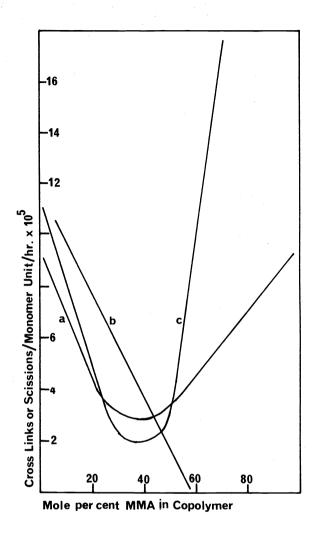


Fig. 2. Rates of chain scission and cross-linking in copolymers of MMA and MA under uv irradiation as a function of copolymer composition. a, chain scission in film; b, cross-linking in film; c, chain scission in solution.

is illustrated by curve c in Fig. 2 from which it is clear that while rates of chain scission in poly(methyl acrylate) and methyl acrylate rich copolymers in film and in solution are comparable, the rate of chain scission in methyl methacrylate rich copolymers is very much greater in solution.

One obvious difference between the methyl acrylate and methyl methacrylate ends of the copolymer composition range is that the glass transition temperatures of high methyl acrylate copolymers are below the ordinary temperatures at which these film and solution photolyses were carried out while the glass transition temperatures of high methacrylate copolymers lie well above ambient temperature. The values of  $T_{\rm g}$  for poly(methyl methacrylate) and poly(methyl acrylate) are 105° and 6°C respectively (Ref. 6). It might thus reasonably be predicted that the immobility of the polymer molecules in high methacrylate copolymers would result in a high proportion of 'cage' recombination of the primary radical products. In solution, on the other hand, these primary radicals would more readily diffuse apart thus explaining the higher rate of degradation in solution. Because, at ordinary temperatures, high acrylate copolymers are above their glass transition temperatures there would be much less tendency to 'cage' recombination of radicals and rates of degradation in film would increase towards rates in solution.

In order to test this theory experiments have been carried out in which the rates of photolytic scission of a high methacrylate copolymer have been measured over a range of temperatures above and below the glass transition point. The glass transition temperature, measured by DTA, is 82°C and Fig. 3 illustrates the rapid increase in the rate of photolytic

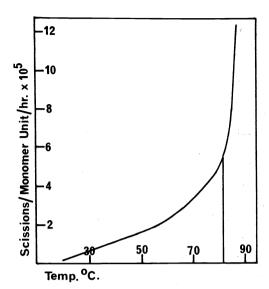


Fig. 3. Dependence on temperature of rate of chain scission by uv radiation of a 70/30, MMA/MA copolymer.

scission which occurs in the vicinity of this temperature.

These experimental data on polymethacrylates and polyacrylates illustrate how many factors, including structure, mode of initiation, temperature, physical properties and impurity comonomers may all play a significant role in determining the course of a degradation reaction so that one must not be tempted to attribute a unique degradation process to a polymer on the basis of limited experimental investigation and comparison with materials with similar structures.

### POLYSILOXANES

The siloxane polymers provide further evidence of the influence of small changes in structure on polymer stability, in particular the replacement of methyl by phenyl substituents. The TG curves 1-5 in Fig. 4 (Ref. 7) for a number of poly(dimethylsiloxanes),

give an impression of their level of stability while curve 6 which refers to polymer 2 with 5% added KOH demonstrates how this material, which is often used industrially as a polymerisation catalyst, will cause drastic instability.

As normally prepared, these polysiloxane molecules are terminated by hydroxyl groups but they may be 'end capped' by replacing the hydroxyl groups by trimethylsilyl structures by treating the polymer with hexamethyldisilazane,

$$\begin{array}{c}
\text{CH}_{3} \\
\text{Si} - \text{OH} + (\text{CH}_{3})_{3}^{\text{Si}} - \text{N} = \text{N} - \text{Si}(\text{CH}_{3})_{3} \xrightarrow{\text{CH}_{3}} \\
\text{CH}_{3}
\end{array}$$

$$\begin{array}{c}
\text{CH}_{3} \\
\text{Si} - \text{O} - \text{Si}(\text{CH}_{3})_{3} \\
\text{CH}_{3}
\end{array}$$

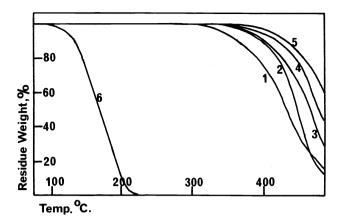


Fig. 4. TG traces of various dimethylsiloxanes. Molecular weights: 1, 94,500; 2, 111,500; 3, 183,000; 4, 258,000; 5, 111,500 end capped; 6, 111,500 with 5% KOH. Heating rate, 10° min<sup>-1</sup> under dynamic nitrogen.

Comparison of curves 2 and 5 shows how end capping enhances stability. In general also the TG curves indicate increased stability with increasing molecular weight (a lower concentration of terminal structures) (curve 1, 94,000; curve 4, 258,000). These effects of molecular weight and end capping clearly demonstrate that the degradation of hydroxyl terminated polymers must be associated with chain ends and the fact that the series of cyclic oligomers is the only product leads to the mechanism,

which illustrates the formation of trimer although tetramer, pentamer, etc. are formed by reaction of the hydroxyl group at silicon atoms further along the chain.

Although end blocking imparts stability on the polymer, the products are the same as for hydroxyl terminated polymers and a comparable mechanism may be suggested,

in which a second silicon atom replaces the hydrogen atom in the four membered ring transition state.

It is suggested that acceleration of the degradation reaction by KOH is due to hydroxyl ions providing the driving force for the oligomer forming reaction.

The incorporation of phenyl groups is used in some commercial silicones to improve thermal stability. The principal effects may be observed by studying poly(methylphenylsiloxane),

Two very obvious differences from the dimethyl polymer are immediately evident (Ref. 8). Firstly, benzene is formed in small amounts, and secondly, the polymer becomes insoluble on heating even at temperatures below  $150\,^{\circ}\text{C}$ .

TG traces 1-4 in Fig. 5 demonstrate that for hydroxyl terminated polymers there is a clear

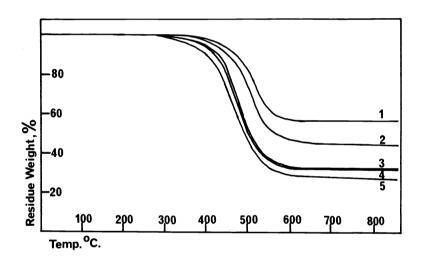


Fig. 5. TG traces for various poly(methylphenylsiloxanes). Molecular weights: 1, 55,700; 2, 121,000; 3, 200,000; 4, 211,000; 5, 200,000 end blocked. Heating rate  $10^{\circ}$  min<sup>-1</sup> under dynamic nitrogen.

correlation between stability and molecular weight, the higher the molecular weight the lower the stability. Comparison of traces 3 and 5 demonstrates, on the other hand, that stability is decreased by end blocking. These effects of molecular weight and end blocking are the exact reverse of the behaviour of poly(dimethylsiloxane). Nevertheless these observations again show a clear involvement of chain ends in the degradation process. Fig. 6 shows that the rate of formation of benzene also decreases with increasing molecular weight.

A typical glc trace of the main products of degradation of poly(methylphenylsiloxane) is shown in Fig. 7. Mass spectral analysis demonstrates that a and b are due to cyclic trimers, d, e, f, and g to tetramers and i to pentamer. Various trimers and tetramers are possible and may be distinguished by nmr spectroscopy as shown in Table 2. The peaks c and h in Fig. 7 are of particular interest. The parent ions in their mass spectra appear at m/e 466 and 602 and in view of the additional evidence of the formation of benzene, cross linking and their positions in the chromatogram it is suggested that they have the following structures.

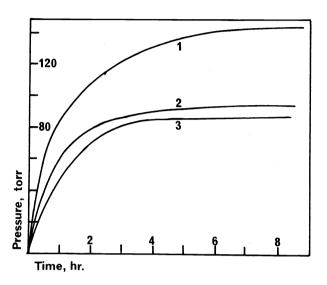


Fig. 6. Effect of molecular weight on the evolution of benzene from poly(methylphenyl siloxanes) heated isothermally at 500°C. 1, 55,700; 2, 121,000; 3, 200,000.

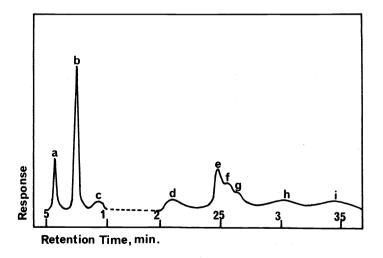


Fig. 7. Glc trace of products of degradation of poly(methylphenylsiloxane). 1% OV1 column at 200° for 10 min, thereafter heated at  $2^\circ$  min<sup>-1</sup> to  $250^\circ$ C.

TABLE 2. Nmr shifts of products of degradation of poly(methylphenylsiloxane)

Structure	Methyl Shift, τ	Mole %
I p	9.484	16.5
II 2 1 2	1. 9.622 2. 9.557	46.7
III PPP	9.519	5.8
IV P 3 1 2	1. 9.852 2. 9.608 3. 9.598	18.0
$V \stackrel{P}{\underset{P}{\longmapsto}} P$	9.719	10.3
IX PPP	9.743	2.7

Since hydroxyl terminal structures confer greater stability than trimethylsiloxy structures and since the production of benzene depends upon the number of hydroxyl groups, it is proposed that the principal effect of hydroxyl groups is to assist cleavage of Si-Ø bonds.

Since this reaction also introduces branching into the polymer it will also account for the development of insolubility and the large residue.

Since the formation of cyclic oligomers is not to be associated with chain terminal structures, the mechanism previously proposed for poly(dimethylsiloxane) seems most reasonable.

At higher temperatures much more benzene is produced than can be accounted for in terms of hydroxyl chain ends. 
The following radical process has been suggested.

Subsequent degradation of polymer incorporating these structures would account for the two degradation products c and h revealed by mass spectrometry.

## POLYURETHANE

My final example is taken from the field of polyurethane degradation and relates to the fire hazard which exists in the commercial application of these materials. Inflammability is not the only problem however. People do not normally die in fires as a result of burning.

Instead they are usually suffociated by smoke and fumes. Every major fire takes a well defined route across a room or through a building depending upon the situation of open doors and windows and the general architecture of the building. The heat generated by the burning material will decompose unburnt polymer ahead of the flame front so that the air is laden not only with products of combustion, but also the unburnt products of thermal decomposition. In order to control the inflammability of commercial materials, fire retarding additives are frequently used. These additives may alter the course of the decomposition process so that the nature of the volatile products, and hence their toxicity, may be radically altered.

Phosphates are frequently used as fire retardants for polyurethanes and the products of thermal decomposition of a sample of polyurethane derived from 1,4-butanediol and methylen-bis-(4-phenyl isocyanate)

HO - 
$$(CH_2)_4$$
 - OH + O = C = N -  $(CH_2)_N$  = C = O

$$\longrightarrow \quad \text{$\sim$0 - $(CH_2)_4$- $0 - $C - $N$} \xrightarrow{\text{$N$}} \quad \text{$CH_2$} \xrightarrow{\text{$N$}} \quad \text{$N$} - C \xrightarrow{\text{$N$}}$$

in presence and absence of ammonium polyphosphate are listed in Table 3 (Refs. 9 and 10).

TABLE 3. Products and structural changes on degradation of polyurethane

Pure Polyurethane	Polyurethane + Ammonium Polyphosphate	
Butane diol (monomer) (BD)	absent	
Methylene bis-(4-phenyl isocyanate (monomer) (MBPI)	reduced	
Carbon dioxide	present	
Butadiene (minor)	absent	
Tetrahydrofuran	increased	
Dihydrofuran (minor)	absent	
Water	present	
Hydrogen cyanide (minor)	absent	
Carbon monoxide (minor)	absent	
Disappearance of urethane link	present	
Formation of carbodiimide	reduced	
Formation of urea structures	present	
absent	aniline	
absent	formaldehyde	
absent	C = N structures	
absent	P - O - C structures	
absent	large residual char	

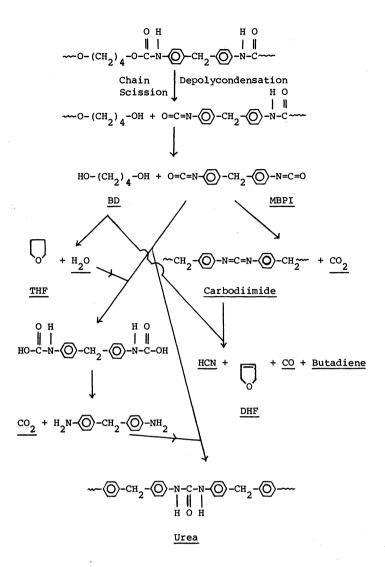


Fig. 8. Mechanism of decomposition of pure polyurethane.

It is clear that the addition of the fire retardant has a profound effect on the reaction but there are two features of particular interest from the fire retarding point of view. Firstly, the fire retardant induces the formation of a large residual char. This has the effect of insulating the decomposing polymer from the feedback of heat from the burning gases. It also implies that very much less volatile inflammable gases are formed. Secondly, the fumes produced in presence of the fire retardant are made much more obnoxious by the presence of the large proportion of aniline. These two opposing features highlight the dilemma frequently encountered in the use of fire retardants, namely, lower inflammability versus more toxic fumes.

All the products of decomposition of the pure polyurethane mentioned in Table 3 can be accounted for in terms of the reaction sequence shown in Fig. 8. It is clear from the mechanism presented in Fig. 9 that the effect of ammonium polyphosphate, or the polyphosphoric acid derived from it, is to drive the reaction in new directions to give desirable cross linking and undesirable aniline formation.

Although I have only cited a limited number of examples, I believe they are representative in illustrating the more important ways in which degradation processes may be modified by relatively minor alterations to the system.

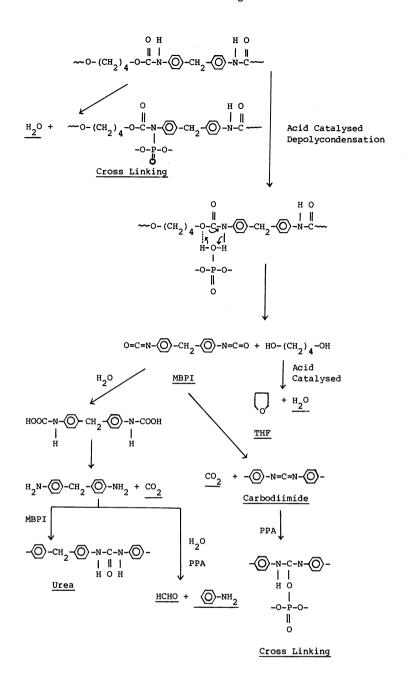


Fig. 9. Mechanism of decomposition of polyurethane in presence of ammonium polyphosphate.

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