# Thermal Degradation of Polymer Mixtures. I. Degradation of Polystyrene–Poly(methyl Methacrylate) Mixtures and a Comparison with the Degradation of Styrene–Methyl Methacrylate Copolymers

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## Synopsis

The degradation behavior of mixtures of polystyrene and poly(methyl methacrylate) in the form of thin films cast from a solution containing both polymers has been compared with that of the individual polymers and of copolymers of the same monomer pair by means of thermal volatilization analysis (TVA) together with product analysis by gas–liquid chromatography determinations of the molecular weight of the solid polymer residues. The results indicate no interaction between the polymers when degraded together. The polymer mixtures are readily distinguished from copolymers of the same overall composition by TVA.

## INTRODUCTION

Over a number of years the degradation behavior of various homopolymers and of certain copolymer systems has been studied in these laboratories. In view of the increasing commercial importance of blends of polymers it is of interest to extend these investigations to the examination of polymer mixtures, particularly in those cases in which the mechanism of degradation of each of the polymers and the copolymers of the same monomer pair has already been established.

One system which falls into this category is that derived from styrene (S) and methyl methacrylate (MMA). The degradation of polystyrene (PS) has been studied extensively both here and elsewhere, and the main features in the breakdown have been established, although on several aspects uncertainty remains. Work up to 1962 has been reviewed by Wall and Flynn,[1] and there have been several further contributions to this problem.[2-7] The mechanism of degradation of poly(methyl methacrylate) (PMMA) is now very well understood; it has been studied by a number of workers, as listed conveniently in a recent study by Jellinek and Luh.[8] The behavior on degradation of copolymers containing various ratios of S to MMA has been the subject of investigations by Grassie and Farish[9] and by McNeill.[10]

In comparing the behavior of polymer mixtures with that of the individual polymers and of copolymers a convenient experimental approach is the recently developed technique of thermal volatilization analysis (TVA).[11,12]  The TVA thermogram for a polymer sample is particularly sensitive to small changes in the structure which affect the degradation mechanism.  This is well illustrated in the case of poly(methyl methacrylate) itself.[10]  It would be expected, therefore, that any effect of one polymer on the other in the mixture during degradation would be clearly reflected in the TVA thermogram.  In the work reported the TVA data have been supplemented by measurements of the number-average molecular weight of the solid residue and by analysis of the volatile degradation products by gas–liquid chromatography (GLC).

## EXPERIMENTAL

### Preparation of Polymers and Copolymers

**Poly(methyl Methacrylate).**  The monomer (I.C.I. Ltd.) was washed twice with alkali, to remove inhibitor, washed thoroughly with distilled water, and dried over calcium chloride.  It was degassed and twice distilled on a high-vacuum line, only the middle fraction being used, finally into a calibrated dilatometer containing sufficient azodiisobutyronitrile (Eastman Kodak) to give 0.7% w/v in the solution.  The dilatometer was sealed under vacuum, and polymerization was carried to 10% conversion at 60°C.  The mixture was then added to 100 ml. of toluene, and the polymer was precipitated from 1 liter of methanol.  The polymer was reprecipitated three times and dried in a vacuum oven at 50°C. for 24 hr.

**Polystyrene.**  The monomer (Forth Chemicals Ltd.) was purified and polymerized by a procedure similar to that described above, except that the initiator concentration was 0.05% w/v and the conversion was 15%.  The mixture was then added to an equal volume of dioxane, and the polymer was precipitated from methanol.  Three reprecipitations from dioxane solution were carried out, and the polymer was finally dried as described above.

**Copolymers.**  The copolymers subsequently referred to were those prepared previously by Grassie and Farish.[9]

### Molecular Weight Measurements

The number-average molecular weights of the undegraded polymers, individually and as a 1:1 mixture by weight, and of the solid residues resulting from partial degradation were measured in toluene solution with a Mechrolab Model 501 Osmometer with a cellophane membrane.

### Thermal Volatilization Analysis

The apparatus used was as described by McNeill.[12]  A standard heating rate of 10°C./min. was used in temperature-programmed runs, and iso-

thermal degradations were also carried out at selected temperatures in the same apparatus. All samples were examined as thin films deposited on the flat base (area, 10 cm.²) of the glass degradation tube from small volumes (<2 ml.) of solutions in Analar-grade benzene. For the mixed polymer samples the films were prepared from single solutions containing both polymers. Solvent was removed in film preparation by blowing nitrogen slowly over the surface of the solution and finally placing the tube in a vacuum oven at 60°C.

## Collection and Analysis of Volatile Products

In the early stages of each experiment, as the temperature was raised, all films lost some traces of residual solvent. By means of the parallel-trap system already described[12] this was collected in one of the two U tubes of the apparatus. The path of the volatile products was then directed to the other U tube, without interruption of the degradation, and the products of degradation were collected. From the design of the apparatus the products collected consisted only of materials volatile at ambient temperature under vacuum. After completion of the degradation these products were distilled into a small collection tube prior to GLC investigation. A Microtek Model GC 2000-R chromatograph was used with a 10 ft. column of S.E. 30 (Applied Science Labs. Inc.) on Embacel (May and Baker Ltd.) at 60°C. and nitrogen as carrier gas.

## RESULTS AND DISCUSSION

The degradation behavior of MMA and S homopolymers is similar in so far as both give large amounts of monomer by unzipping. In the latter case, however, the presence of the tertiary hydrogen atom leads to considerable amounts of transfer, with the result that the products include dimer, trimer, etc., besides monomer. The thermal stability of PMMA is extremely sensitive to the nature of the end structures, initial molecular weight, and the presence of comonomers, even in quite low concentrations. This is well reflected in differences in the TVA thermograms, as discussed in a recent paper.[10] On the other hand, PS samples prepared by several different mechanisms and having different end structures and quite widely different molecular weights show essentially the same behavior as regards rate of production of volatile products. This again is reflected in the fact that the TVA thermograms for such samples are nearly identical.[13]

Copolymers of S and MMA have been degraded by Grassie and Farish,[9] who used an isothermal approach and the dynamic molecular still of Grassie and Melville, and also by NcNeill,[10] who used TVA. Although the behavior of the copolymers is intermediate between that of the individual homopolymers, the presence of S is found to have a disproportionate stabilizing effect on the methyl methacrylate polymer chain. Two factors have been suggested to account for this effect. Grassie and Farish argued that the copolymers possess fewer unstable chain ends than PMMA
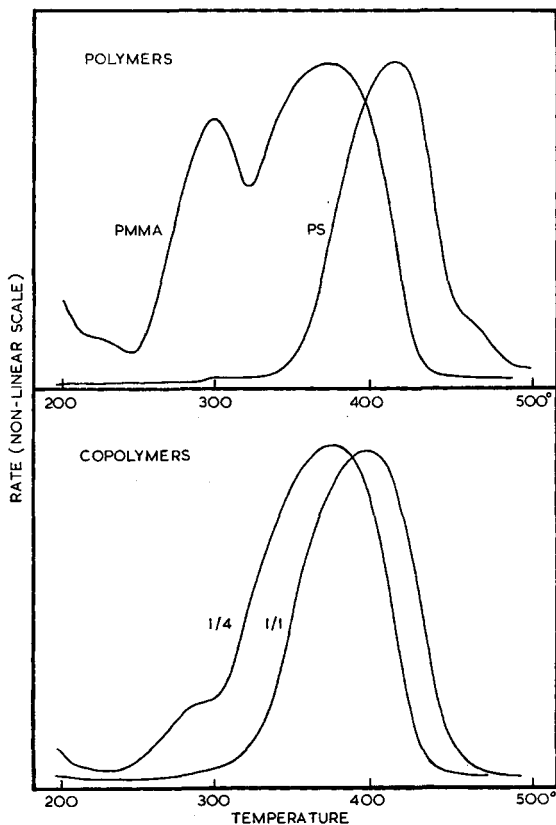
Fig. 1. TVA thermograms for polystyrene, poly(methyl methacrylate), and 1:4 and 1:1 copolymers of styrene and methyl methacrylate (25 mg. samples as thin-film from benzene solution; heating rate, 10°C./min.; temperatures quoted are sample temperatures).

because of a favoured cross-termination step in the copolymerization. McNeill has argued further that there is reason to suspect that a cage effect operates when a pair of polystyryl radicals are produced after an initial scission between a pair of MMA units in the copolymer chain, preventing further unzipping. As a result of these features the TVA thermograms for S/MMA are not simply an 'average' of the thermograms for the corresponding homopolymers. This is illustrated in Figure 1, in which the thermograms for the PS and PMMA samples prepared in this investigation are compared with those of S/MMA copolymers.

Before the results obtained for the polymer mixtures are discussed, consideration may be given to ways in which interaction might occur during degradation.

**Attack of a PS Radical on a PMMA Molecule.** Since the PMMA molecule possesses no tertiary hydrogen atoms vulnerable to attack in the main chain, this reaction would only be expected at chain ends. In view of

the low concentration of ends and of PS radicals at temperatures at which PMMA is already degrading rapidly such an effect is highly unlikely.

**Mutual Reaction of PS and PMMA Radicals.**  If this were to occur, the degradation characteristics of each homopolymer would be altered.

**Attack of a PMMA Radical on a PS Molecule.**  The PS molecule is vulnerable to transfer reactions at the tertiary hydrogen atoms.  Intramolecular transfer occurs extensively in PS degradation.  Although intermolecular transfer is commonly postulated in theoretical treatments of PS degradation,[14] good cases for and against its occurrence can be made on the basis of experimental evidence, and some doubt about its occurrence remains.  If intermolecular transfer occurred in the mixture between a PMMA radical and a PS molecule, decomposition of the initially
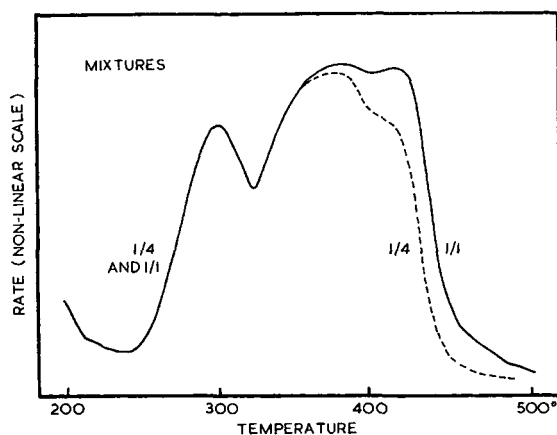


Fig. 2. TVA thermograms for 1:4 (6 mg. and 24 mg.) and 1:1 (25 mg. and 25 mg.) mixtures of polystyrene and poly(methyl methacrylate)( thin film from benzene solution; heating rate, 10°C./min.; temperatures quoted are sample temperatures).

formed tertiary radical could lead to the formation of volatile products from PS at temperatures below those at which this polymer normally degrades.

Since PMMA degrades at considerably lower temperatures than PS, if any interaction were to occur, the last reaction would provide the most probable route.  In recent work on the degradation of polystyrene–poly-(α-methyl styrene) mixtures Richards and Salter[7] found that PS degradation could be initiated by a transfer reaction at temperatures below those at which PS normally degrades.  They concluded, however, that the radical responsible was not a poly(α-methyl styrene) radical but a monomeric α-methyl styrene radical resulting from depolymerization.

Thermograms for 1:4 and 1:1 mixtures of PS and PMMA are reproduced in Figure 2.  It is clear that these represent simply the behavior to be expected, if each polymer degraded independently of the other, and there is no indication whatever of any interaction under the conditions used.

There remains the possibility, however, of some interaction occurring which would not be reflected in the overall rate of volatile production, as determined by TVA. Thus, conceivably, the S/MMA ratio in the products at a given temperature of degradation could differ from that expected, or molecular weight changes might take place. In pursuit of these possibilities the products from isothermal degradation experiments, with the same apparatus, were examined by GLC, and the number-average molecular weights of the solid polymer residues from partial degradation were determined by osmometry. The temperatures for these isothermal studies were carefully chosen. At 290°C. PMMA is undergoing quite rapid end-initiated depolymerization, whereas PS is scarcely degraded at all. At 320°C., however, the end-initiated reaction in PMMA is quickly completed, and the residual polymer is degrading by depolymerization initiated by random scissions, while PS is degrading at an appreciable rate. Thus, at 290°C. any effect of PMMA on PS degradation should be manifest, whereas at 320°C. the possibility of an effect of PS on PMMA degradation may also be considered. The results obtained are collected in Table I.

TABLE I
Isothermal Degradation Data

| Sample[a] | Mol. wt. | Volatiles, % of sample wt. | Compn. of volatiles |
|---|---|---|---|
| PS undegd. | 228,000 | — | — |
| PS degd. at 290°C., 30 min. | 228,000 | nil | — |
| PS degd. at 320°C., 30 min. | 39,000 | 25 | Mainly styrene |
| PMMA undegd. | 134,000 | — | — |
| PMMA degd. at 290°C., 30 min. | 120,000 | 40 | MMA |
| PMMA degd. at 320°C., 30 min. | 101,000 | 75 | MMA |
| 1:1 mixture undegd. | 167,000 | — | — |
| 1:1 degd. at 290°C., 30 min. | 131,000 | — | MMA only |
| 1:1 degd. at 320°C., 30 min. | 70,000 | — | ≈1:3 S/MMA |

[a] Degd. and undegd., degraded and undegraded, respectively.

The product analysis by GLC after calibration experiments on the same column, with pure monomers and mixtures, enabled the following conclusions to be drawn.

(1) At 290°C. there is no significant degradation of PS producing volatile products, when PS is heated for 30 min. in the presence of an equal amount of PMMA.

(2) At 320°C. the ratio of products from degradation of the mixture for 30 min. is as would be expected, if there were no interaction between the polymers. The ratio of products is approximate, however, and does not preclude the possibility of a small effect which might pass undetected.

Thus, the product analysis data confirm the conclusion already reached from the TVA thermograms. The results of the molecular weight measurements are also constant with this view, although the molecular weight drop

for the mixture at 290°C. is marginally larger than expected. Any significant amount of intermolecular transfer between PMMA radicals and PS molecules, however, would result in a substantial drop in the molecular weight of the residue; this has not been observed.

All three sets of data, therefore, in this investigation point to the conclusion that, when PS and PMMA are degraded as a mixture in the form of a thin film, there is no detectable interaction between the polymers.

Since TVA thermograms for the mixed-polymer system are totally different from those for copolymers of similar overall composition, TVA provides a convenient method of distinguishing blends of these polymers from copolymers. Another example of the use of TVA for this purpose has recently been given by McGaugh and Kottle[15] for the case of ethyl acrylate–ethylene polymer mixtures and copolymers.

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