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The thermal degradation of poly(allyl methacrylate)

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The thermal degradation of poly(allyl methacrylate) has been investigated using thermal volatilisation analysis (TVA), thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The main pyrolysis products have been identified and the characteristics of the reactions deduced and discussed. Mechanisms have been proposed to account for the products formed. © 1996 Published by Elsevier Science Limited

1 INTRODUCTION

The polymerisation of allyl methacrylate has been studied previously. This polymerisation takes place mainly through the methacrylate groups.[1] The dielectric properties and thermal stability of cross linked copolymers of allyl methacrylate and methyl methacrylate have also been examined.[2,3] The thermal stability of the poly(allyl methacrylate) and the processes involved in its thermal breakdown however, have not been studied previously. The present investigation is a detailed study of the thermal degradation and the volatile products formed during the thermal degradation of poly(allyl methacrylate).

2 EXPERIMENTAL

Allyl methacrylate (AMA) (Aldrich) was washed twice with 5% aqueous sodium hydroxide to remove inhibitor, washed thoroughly with distilled water, and dried over anhydrous calcium chloride. It was degassed and distilled on a high vacuum line, only the middle portion being used. α,α-Azobisisobutyronitrile (AIBN) (E-Merck) was recrystallised from absolute methanol and dried under vacuum at room temperature.

2.1 Polymerisation

Poly (allyl methacrylate) was prepared by bulk polymerisation of the monomer under vacuum at 60°C with 0.05% w/v AIBN as initiator. The extent of polymerisation was indicated by the reduction in total volume and increase in viscosity content. The polymer was precipitated in methanol, purified by reprecipitation in methanol from acetone solution and dried in a vacuum oven at room temperature for 48 h. The number average molecular weight was 16 000.

2.2 Degradation studies

Experimental methods include thermogravimetry (TG), derivative thermogravimetry (DTG), differential thermal analysis (DTA) and thermal volatilisation analysis (TVA).[4,5] The products of degradation were separated by TVA into non-condensable gases, condensable gases and liquids, cold ring fraction (CRF) (products volatile at degradation temperature but not at ambient temperature) and residue. The non-condensable gases were identified by means of an on-line mass spectrometer. The condensable gas/liquid fraction was further separated by subambient TVA (SATVA)[6] into several frac-

tions: the more volatile fractions were examined as gases by FTIR spectroscopy and mass spectrometry (MS) and the less volatile liquid fraction was further examined by GC-MS. The CRF was studied by FTIR spectroscopy.

3 RESULTS AND DISCUSSION

The TVA behaviour of PAMA is illustrated in Fig. 1(a) which shows that breakdown occurs in two steps, with rate maxima at 276°C and 409°C. In the first stage of degradation only 0°C and −45°C traces show a response which implies that relatively high boiling products are being evolved which may be the monomer allyl methacrylate. In the second stage of degradation the separation of 0°C, −45°C, −75°C, −100°C and −196°C traces indicate the presence of products of various volatilities including non-condensable gases.

TG, DTG and DTA curves for PAMA are shown in Fig. 2. The polymer is thermally stable up to about 210°C and two stage break-down is confirmed. The first stage accounts for about
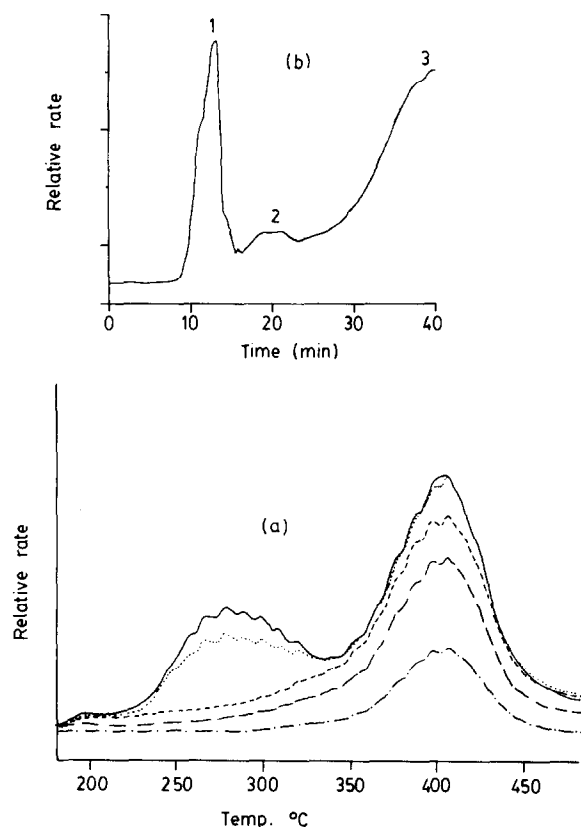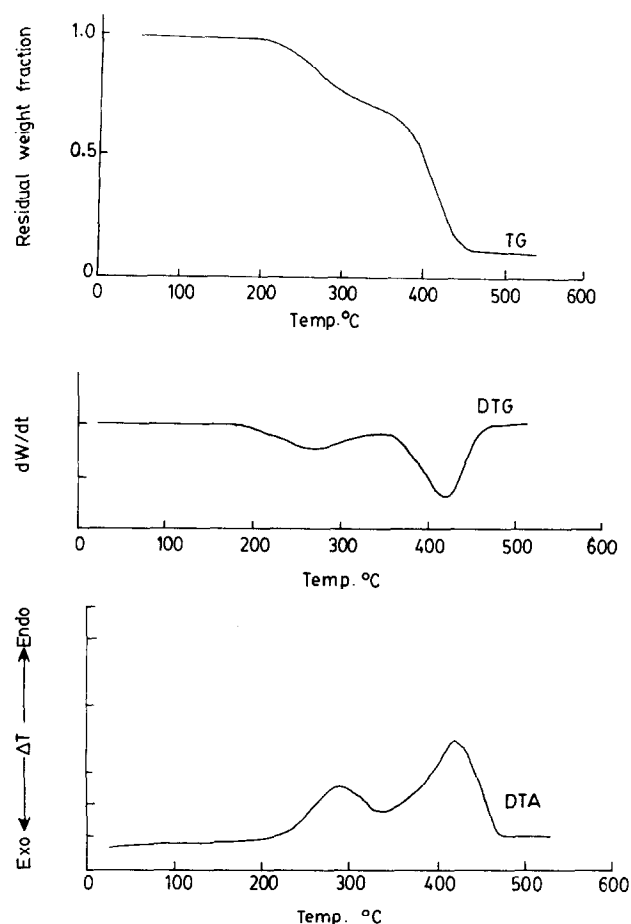
Fig. 2. TG, DTG and DTA curves for PAMA (dynamic N₂, 10°C min⁻¹).

35% of weight loss. Overall weight loss for PAMA is about 98% at 500°C. The DTG behaviour parallels the TVA behaviour by showing D_{max1} at 270°C and D_{max2} at 420°C. The activation energies for the thermal degradation were calculated using Horowitz's[7] method and found to be 12.67 and 31.4 Kcal/mol, respectively. The DTA curve for PAMA shows two endotherms, the first at 290°C and the second at 418.9°C. The DTA data are consistent with the TG, DTG and TVA results.

3.1 Characterisation of volatile products

The SATVA trace for warm-up from −196 to 0°C of the condensable volatile product fraction from degradation in the TVA apparatus up to 500°C is shown in Fig. 1(b). The condensable gaseous products and liquid fraction were examined by FTIR and MS. The results are presented in Table 1. The first SATVA peak was mainly due to carbon dioxide together with small amounts of propene and dimethyl ketene. The

Fig. 1. (a) TVA curves (vacuum, 10°C min⁻¹) for PAMA. ———, 0°C; · · ·, −45°C; - - -, −75°C; — — —, −100°C; − · −, −196°C. (b) SATVA curve for separation of condensable volatile degradation products of PAMA.

Table 1. Product assignments for the SATVA separation of Fig. 1(b)

SATVA peak	Product name	IR (cm⁻¹)	MS (m/z)
(1)	Carbon dioxide	3702, 2360, 688	44, 28, 16, 27
	Propene	3130, 2980, 2970, 1665, 1470, 1380, 990, 910	42, 41, 39, 27
	Isobutene	3090, 2950, 1660, 890	41, 56, 39, 28, 27, 55.
	Dimethylketene	2170, 2140.	
(2)	Acrolein	3030, 2780, 2700 2630, 1700, 1410 1150, 980, 920	27, 56, 25, 55, 28, 26, 29, 18
(3)	Diallylether	—	41, 39, 42, 69, 54, 56, 57, 83 27, 98
	Allyl methacrylate	2940, 1720, 1640, 1450, 1410, 1370, 1320, 1300, 1160, 1010, 990 940, 810	41, 69, 78 39, 81, 101 52, 126

second small peak was due to acrolein. The third peak comprised mainly the monomer and diallylether. The liquid fraction, at the third peak was subjected to GC-MS for further investigation. The GC-MS (with peak assignments) chromatogram of the liquid fraction from the degradation of PAMA to 500°C under normal TVA conditions is shown in Fig. 3.

3.2 Analysis of the cold ring fraction (CRF)

The CRF which resulted from degradation of the PAMA to 500°C under TVA conditions was examined by FTIR spectroscopy and is compared with undegraded PAMA in Fig. 4. In most respects these spectra are similar, indicating that the CRF consists essentially of polymer chain

fragments. The CRF spectrum shows additional peaks, however, at 1019, 1764 and 1805 cm⁻¹, which are typical of a six-membered ring structure.[8] A new C=O peak appears at 1709 cm⁻¹ with its overtone above 3200 cm⁻¹ and a band at 1165 cm⁻¹, suggesting the formation of an aliphatic ketone in the vicinity of unsaturation.

3.3 Non-condensables

The separation of the −196°C trace in the TVA curve indicates that non-condensable gases are formed during the second degradation stage. All the non-condensable gases (CH_4, CO, H_2) are thought to result from decompositions of anhydride structures and ester groups and the reaction product of the CH_3 radical.
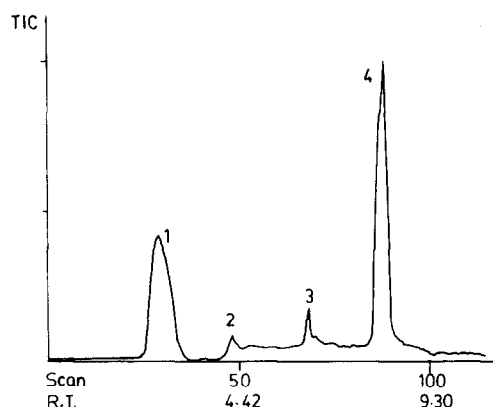

Fig. 3. GC-MS chromatogram of liquid fraction from degradation of PAMA to 500°C under TVA conditions. Assignments: (1) allyl methacrylate, (2) diallylether, (3) unknown, (4) AMA dimer.
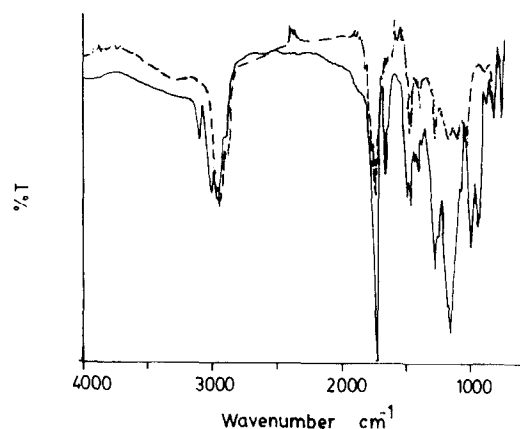

Fig. 4. FTIR spectra of undegraded PAMA (———) and CRF of PAMA (— — —).

3.4 Analysis of residue

Heating PAMA to 330°C at 10°C min^{-1} produced a light yellow residue which was insoluble in common organic solvents. The spectral changes induced by partial degradation were examined by FTIR spectroscopy. The spectrum of the degraded polymer shows indications (peaks at 1026, 1760 and 1803 cm^{-1}) of anhydride structures.[8,9] The development of absorption at 1706 cm^{-1} with an overtone above 3200 cm^{-1} and a band at 1160 cm^{-1} suggests the formation of α–β unsaturated ketone.[9]

4 DISCUSSION

The basic features of the thermal degradation mechanism of PAMA may be summarised as follows.

The monomer is the major product of degradation. Monomer formation at lower temperature is probably due to initiation at unsaturated chain ends, whereas monomer formation in the region of 300–400°C is probably associated with initiation following scission of the backbone at various points.
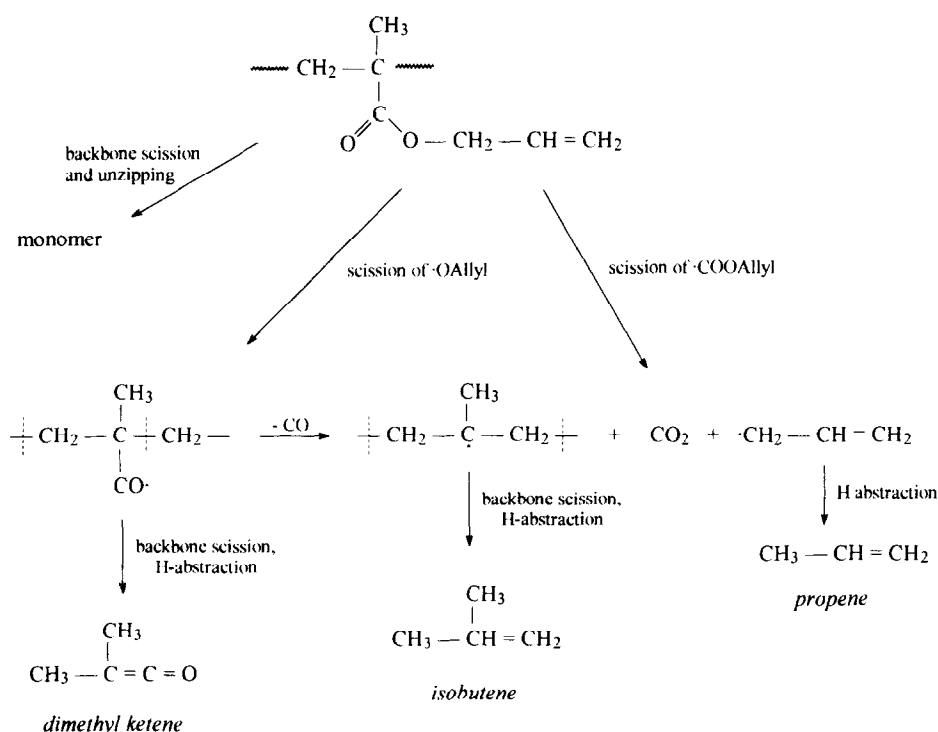
The nature of the minor products of degradation also indicates that side group scission

processes compete to some extent with backbone scission and unzipping. There are two main possibilities for scission in the side group, and these scissions lead subsequently to the formation of propene, isobutene and dimethyl ketene, together with CO and/or CO_2.
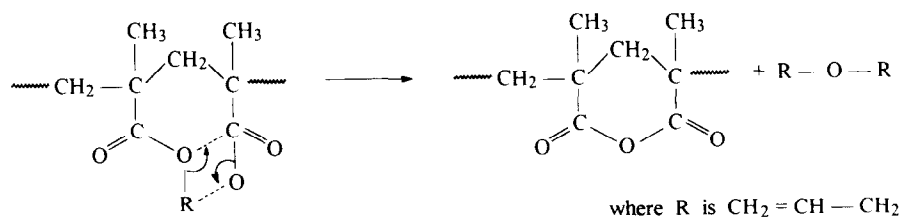
All of the above processes are summarised in Scheme 1.

The formation of diallyl ether and the presence of anhydride rings in the partially degraded polymer at 330°C and in the CRF indicate that an intramolecular cyclisation of adjacent monomer side groups is also possible. A suggested route involving a four-centre transition state is shown in Scheme 2.
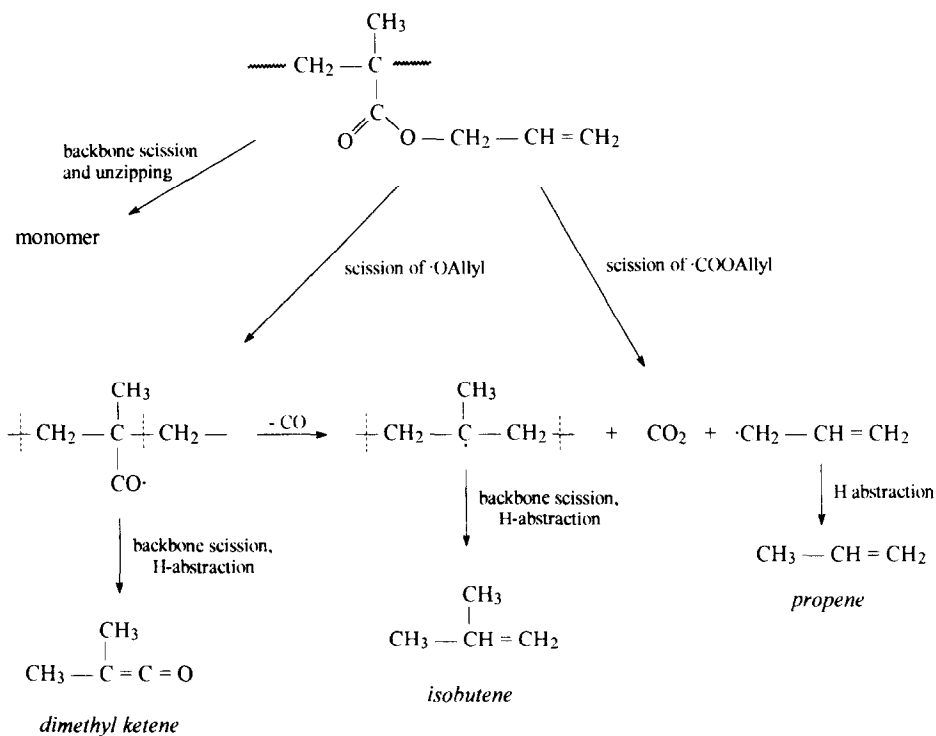
At higher temperatures, breakdown of the anhydride rings will occur. Loss of both CO and CO_2 would be followed by backbone scission and H-transfer, giving smaller macromolecules and encouraging cold ring fraction formation, as is observed. An alternative reaction can also be envisaged, however, in which only CO_2 is split out and CH_3 migration and rearrangement produces unsaturated ketone in the chain without scission. This explains the observation in the partially degraded polymer residue where IR absorption suggests the presence of α,β-unsaturated ketone groups. These decomposition processes are shown in Scheme 3.

Scheme 1.

where R is $CH_2 = CH - CH_2$

Scheme 2.

backbone scission
and unzipping

monomer

scission of ·OAllyl

scission of ·COOAllyl

$-CO$

backbone scission,
H-abstraction

backbone scission,
H-abstraction

H abstraction

$CH_3 - CH = CH_2$

propene

backbone scission,
H-abstraction

$CH_3 - C = C = O$

dimethyl ketene

$CH_3 - CH = CH_2$

isobutene

Scheme 3.

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