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THE APPLICABILITY OF DTG TO POLYMERISATION STUDIES

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The application of derivativ thermogravimetry (DTG) to investigate polymerisation mechanisms is illustrated using the radical polymerisation of di-*n*-alkyl itaconates as well as the photoinitiated polymerisation of methyl methacrylate by colloidal CdS. The thermal properties of the resulting polymers are described. The advantages and disadvantages of DTG are discussed.

Keywords: DTG analysis, polymerisation mechanisms, vinylidene type polymers

Introduction

The polymerisation, as well as the non-oxidative thermal stability of poly(methyl methacrylate) (PMMA) have been the subject of many investigations. It is well known that PMMA thermally decomposes by depolymerisation. Generally, the depolymerisation of PMMA can be initiated by the scission of head-to-head bonds, at unsaturated chain ends and by main chain scission. As a consequence, three DTG maxima are registered in the case of PMMA prepared by free radical polymerisation [1]. Grassie and coworkers [2] first suggested that the importance of the different modes of depolymerisation initiation, together with the effect of chain transfer in the polymerisation of MMA can be established by studying the thermal properties of the obtained polymer. Kashiwagi *et al.* have shown that the first two DTG maxima, ascribed to depolymerisation initiated by

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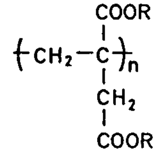
the scission of head-to-head bonds and bonds in the β position to chain end unsaturation can be decreased or completely supressed when PMMA is synthesised in the presence of the chain transfer agent tertiary-butyl mercaptan [1]. PMMA synthesised by anionic polymerisation has been shown to be thermally more stable than PMMA obtained by free radical polymerisation due to the absence of chain end unsaturation and head-to-head structures [3]. In this case only one DTG maximum is observed.

This approach to the study of polymerisation mechanisms has been extended to include poly(di-*n*-alkyl itaconates), which are vinylidene type polymers of the structure:



$$\left(CH_2-\overset{\overset{\displaystyle COOR}{|}}{\underset{\underset{\underset{\underset{\displaystyle COOR}{|}}{\displaystyle CH_2}}{|}}{C}}\right)_n$$

where *R* in an *n*-alkyl group, and to PMMA prepared using colloidal cadmium sulphide as a photoinitiator. The use of this novel initiator results in a chain end structure, the thermal stability of which has only recently been described [4].

Experimental

Diethyl, di-*n*-butyl, di-*n*-hexyl and di-*n*-octyl itaconate (DEI, DBI, DHI and DOI, respectively) were prepared by the standard esterification of itaconic acid (Aldrich, p.a.) with the corresponding alcohol (all Aldrich, p.a.). They were vacuum distilled before use. Dimethyl itaconate (DMI) (Aldrich, p.a.) was recrystallised from methanol. Benzene (Alkaloid, p.a.), toluene, dioxan and chloroform (all Merck p.a.) were distilled before use.

The polymers were obtained by polymerising the monomers either in bulk in the presence or absence of *n*-dodecyl mercaptan (Aldrich p.a.) under high vacuum or in solvent under nitrogen. α, α'-Azobisisobutyronitrile (AIBN) was used as the initiator. The bulk polymerisations were taken to yields of not more than 20%, while the polymerisations performed in the presence of chain transfer agent or in solution were taken to yields not exceeding 5%.

Colloidal cadmium sulphide was prepared by the injection of H_2S gas to a solution of cadmium perchlorate in 1-propanol containing sodium 1-(4'-dodecyl)-benzenesulphonate as stabiliser. Details of the preparation have been given elsewhere [5]. 1-Propanol was removed under vacuum at 35°C and the resulting powder redispersed in MMA. Polymerisation was initiated by irradiating with the 435.8 nm line of a 600 W mercury-xenon lamp. The yield of polymer was about 5%.

The molar masses of the polymers were determined by GPC (Knauer/Trilab) using poly(methyl methacrylate) samples (Röhm GmbH, Germany) as standards.

FTIR absorption spectra were recorded using a Bruker IFS 25 instrument. The samples were prepared as polymer films on KBr pellets.

A Perkin Elmer TGS-2 instrument was used for the thermogravimetric measurements. Non-isothermal experiments were performed in the temperature range 30° to 500°C at heating rates of 2.5 and 10 deg·min^{-1}. The average sample size was 5 mg and the nitrogen flow rate 25 cm^3/min.

Results and discussion

Poly(di-n-alkyl itaconates)

In the absence of oxygen, poly(di-*n*-alkyl itaconates), similarly to PMMA, thermally decompose predominantly by depolymerisation [6]. The volatile non-oxidative thermolysis products consist of approximately 90% monomer and of compounds mostly resulting from side chain scission (such as alcohol, acetate, etc.) [7, 8]. Under the same thermolysis conditions, the composition of the volatile products did not depend on the size of the ester substituent in the investigated range from the dimethyl to the di-*n*-octyl derivative. The shape of the DTG curves of poly(di-*n*-alkyl itaconates) changed progressively with increasing ester substituent size (Fig. 1). The dimethyl (PDMI) and diethyl (PDEI) derivatives were characterised by a single peak with a shoulder which became a plateau in the case of poly(di-*n*-butyl itaconate) (PDBI). Two distinct peaks were registered in the case of the di-*n*-hexyl (PDHI) and di-*n*-octyl derivatives (PDOI). The relative magnitudes, i.e. the shapes, of the DTG peaks did not depend on the molar mass of the polymers as in the case of PMMA.

By comparison to PMMA, the first DTG maximum of poly(di-*n*-alkyl itaconates) was assumed to originate from the depolymerisation of polymer molecules with unsaturated chain ends and the second maximum to the main chain scission initiation of depolymerisation. Head-to-head structures appeared not to be formed in poly(di-*n*-alkyl itaconates). They would have resulted in a DTG peak at lower temperatures than the corresponding peak in the DTG curve of PMMA as the head-to-head bond in poly(di-*n*-alkyl itaconates) should be thermally more labile due to increased steric effects.

The origin of the first DTG maximum was confirmed by synthesising poly(di-*n*-alkylitaconates) in the presence of the chain transfer agent *n*-dodecyl mercaptan. The change in the content of chain end double bonds of PDHI samples

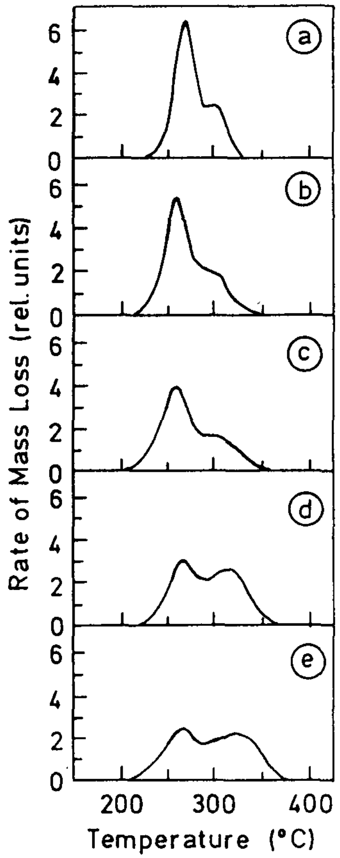


Fig. 1 DTG curves of a) PDMI, b) PDEI, c) PDBI, d) PDHI and e) PDOI, prepared in bulk at 40°C using 0.5 mol% AIBN as initiator, heating rate 2.5 deg·min^{-1}

prepared in the presence of various amounts of *n*-dodecyl mercaptan was registered by absorption FTIR spectroscopy via the change in the intensity of the vinylidene bond stretching vibration (1640 cm^{-1}). The number of double bonds per polymer chain was proportional to the intensity (height) of the peak at 1640 cm^{-1} multiplied by the number average molar mass of the sample. Correspondingly, with increased mercaptan concentration, the relative number of double bonds per polymer chain and the size of the first DTG maximum both decrease (Fig. 2).

The degradation products (acetate, acrylate, CO_2, CO, etc.) [7, 8] indicated that depolymerisation is also, to a small extent, initiated over the whole mass loss range by side chain scission. The initiation reaction was not registered as a separate DTG maximum. As the first DTG maximum was not completely suppressed in the case of PDHI synthesised in the presence of larger amounts of *n*-dodecyl mercaptan (>2 x 10^{-2} mol/dm^3) (Fig. 2b), it may be assumed that a broad flat peak, usually covered by the other two DTG maxima, encompassing the whole mass loss range, could originate from the side chain scission initiation of depolymerisation.

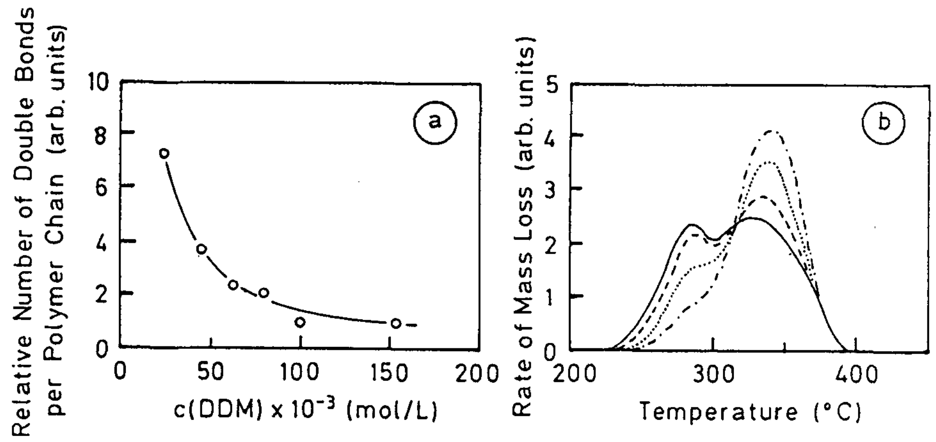


Fig. 2 a) Dependence of the relative number of chain end double bonds on the amount of *n*-dodecyl mercaptan present during the polymerisation of di-*n*-hexyl itaconate; b) DTG curves of PDHI polymerised in the presence of (—) 0, (– – –) 23, (·····) 63 and (·–·–·–) 150 mmol/L DDM, heating rate 10 deg·min^{-1}. All polymers were synthesised in bulk at 60°C under high vacuum using 0.5 mol% AIBN as initiator

The question that arose was that of the origin of the double bonds at the polymer chain ends. Theoretically, in the case of a polymer that completely thermally depolymerises and which preferentially terminates by disproportionation during free radical polymerisation, as was assumed to be the case for poly(di-*n*-alkyl itaconates), two DTG maxima of similar size, originating from the two different depolymerisation initiation modes, should be registered if the depolymerisation dezip length is long enough. In the case of a short dezip length the peak arising from main chain scission initiation of depolymerisation should increase in magnitude relative to the peak arising from chain end initiation of depolymerisation. In the case of the lower poly(di-*n*-alkyl itaconates), however, the first DTG maximum was considerably larger than the second one implying an additional source of chain end unsaturation.

Nagai and Yoshida [9] have suggested that, due to the allylic structure of the monomer, the affinity towards chain transfer to monomer should be considerable in the case of the itaconates. Such chain transfer would involve the abstraction of an allylic hydrogen to terminate the growth of the chain and the formation of a propagating radical with a double bond at its end. DTG supported this hypothesis, the relatively large initial DTG peak originating from the reinitiation of polymerisation after chain transfer has occurred. With increasing ester substituent size the affinity towards chain transfer to monomer during free radical polymerisation is assumed to decrease due to steric reasons [9]. Thus the decrease in the size of the first DTG maximum with increasing substituent size was registered (Fig. 1).

The complete absence of a peak corresponding to head-to-head groups suggests radical-radical polymerisation termination, both by combination and disproportionation, was suppressed during the polymerisation of these monomers. The chain end unsaturation arose mainly from chain transfer to monomer.

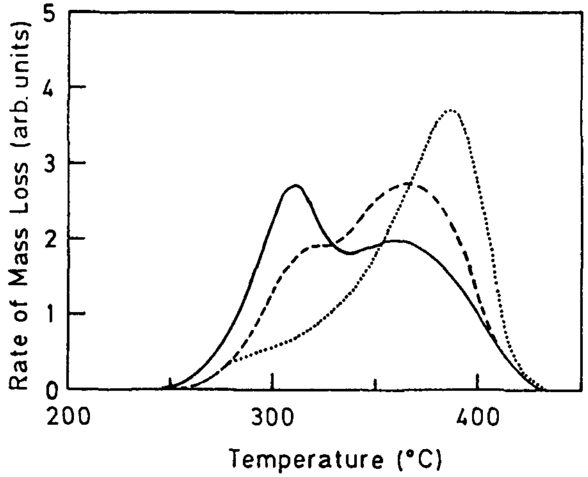


Fig. 3 DTG curves PDBI samples synthesised in benzene under nitrogen at 57°C, heating rate 10 deg·min^{-1}, (—) 0, (- - -) 7.78 and (·····) 9.53 mol/L benzene

In order to further follow the effect of synthesis conditions on the formation of specific chain end structures, a series of PDBIs was synthesised in benzene, which was chosen as the solvent because of its supposed inertness. The DTG curves of these polymers are shown in Fig. 3. In all cases the first DTG maximum decreases with increasing benzene concentration present during the polymerisation. This was the first indication that chain transfer to benzene might be abnormally high in the polymerisation of di-*n*-alkyl itaconates. This was confirmed for the case of DBI where a chain transfer constant to monomer of 1.89×10^{-3} was determined at 57°C. This compares to a value of 1.58×10^{-4} for *n*-butyl methacrylate at 60°C [10].

Similar curves and effects, but more pronounced, were observed for PDBI prepared in toluene, dioxan and chloroform solutions. The magnitude of the effects was found to reflect the determined chain transfer constants to solvent [11].

PMMA prepared using colloidal CdS as a photoinitiator

The initiation of the polymerisation of MMA using colloidal CdS has recently been described [4]. This is a heterogeneous system in which the photogenerated positive hole in the valence band of the semiconductor is assumed to initiate polymerisation. In Fig. 4a the DTG curve of the PMMA sample prepared using colloidal CdS as a photoinitiator is shown together with a free radically prepared sample of comparable molar mass ($\overline{M}_w$ approx. 1×10^5). The first two small DTG peaks confirm the radical mechanism of polymerisation. Using a peak separation program [12], the DTG curve of the PMMA sample prepared using colloidal CdS was separated into its constituent peaks. It was observed that an additional peak, representing a previously unreported depolymerisation initiation mode, was present when the new photoinitiator was used and this new initiation mode was actually the main mode of initiation of depolymerisation. This must represent the scission of a bond intermediate in strength between the bonds β to a terminal unsaturated group, formed during polymerisation as the result of chain termination by disproportionation, and main chain bonds. This new depoly-merisation initiation mode also originated from the scission of a bond in the β position to a terminal unsaturated group, but in this case the β bond was a tail-to-tail bond originating during the initiation of polymerisation by the CdS. A tail-to-tail structure in the β position would be expected to be intermediate in strength to a head-

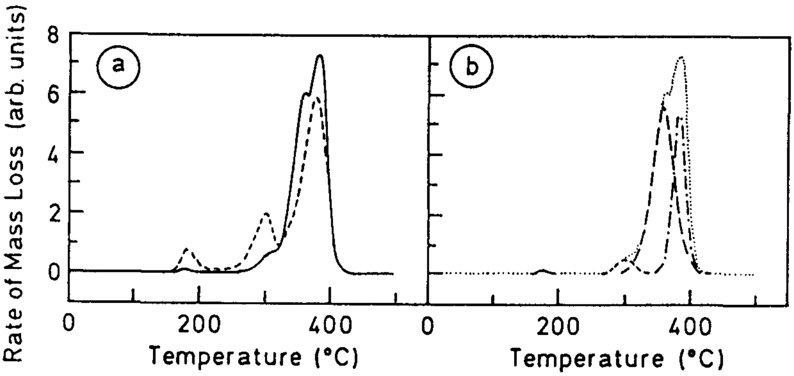


Fig. 4 a) DTG curves of PMMA prepared using colloidal CdS (——) and AIBN (– – –) as initiator; b) Separation of the DTG curve (·····) of the CdS initiated PMMA into its constituent peaks, (——) peak 1, (– – –) 2, (— — —) peak 3 and (—· —) peak 4

to-tail structure in the β position and main chain bonds. Using the information gained from DTGA it was possible to propose an initiation mechanism whereby the positive hole oxidises a MMA molecule by abstracting a hydrogen atom from the α-methyl group. The formed radical, which still contains a double bond, initiates the polymerisation. The result of this initiation mode implies that every chain, assuming the absence of any relevant chain transfer to monomer in the case of MMA, commences with an unsaturated group. The bond in the β position to the double bond in this case is a tail-to-tail bond. The initiation of depolymerisation occurs mainly by the scission of these bonds. The small size of the DTG peaks resulting from depolymerisation initiated by structures originating during polymerisation termination (peaks 1 and 2) suggest that termination in the polymerisation initiated by colloidal CdS is predominantly by chain transfer probably to CdS. This assumption was confirmed by the dependence of the molar mass of the polymers on the CdS concentration [4].

Conclusions

DTG was found to be a useful tool in the analysis of the polymerisation and thermal degradation of poly(di-*n*-alkyl itaconates). It also helped to elucidate the polymerisation mechanism of MMA initiated by colloidal CdS, a new photoinitiator.

DTG could be more commonly used in the analysis of thermally weak structures in polymers that predominantly depolymerise. In analytical techniques such as FTIR and high resolution NMR the presence of thermally weak structures is measured directly. In DTG the effects of the weak structures are magnified as they initiate chain reactions. The detection limit for DTG is, therefore, lower than those of FTIR and NMR. No special purification of the polymers is required for DTG, whereas for FTIR and NMR the polymer samples must be rigorously purified from monomer and other impurites which could affect the very small signals obtained with these techniques. For the successful application of DTG, an indirect detection method, some prior knowledge of the thermal degradation mechanism is required.

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Zusammenfassung — Die Anwendung von DTGA zur Untersuchung von Polymerisationsmechanismen wird anhand der radikalischen Polymerisation von Di-n-alkyl-itakonaten und der fotoinitiierten Polymerisation von Methylmethacrylat mittels kolloidalem CdS dargestellt. Die thermischen Eigenschaften der erhaltenen Polymere werden beschrieben. Es werden Vor- und Nachteile von DTGA diskutiert.