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THERMOGRAVIMETRIC CHARACTERISATION OF POLY(METHYL METHACRYLATE) PHOTOPOLYMERISED BY COLLOIDAL CADMIUM SULPHIDE

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Abstract

The thermal stability of poly(methyl methacrylate) (PMMA) photopolymerised using colloidal cadmium sulphide as the photoinitiator was studied by thermogravimetry (TG) and differential TG (DTG).

The thermal stability of the CdS initiated PMMA was greater than that of conventional radically polymerised PMMA and approached that of anionically prepared PMMA. The DTG curve of the CdS initiated PMMA was a composite of four peaks, three of which correspond to the three peaks observed in the DTG curve of standard radically prepared PMMA. It is suggested that the additional peak arises from a new mode of depolymerisation initiation, that is, from chain end unsaturation introduced into the polymer chain during polymerisation initiation with the colloidal CdS.

Keywords: characterisation, colloidal CdS, photopolymerisation, poly(methyl methacrylate), thermogravimetry

Introduction

The field of colloidal semiconductors has, in recent years, received increased attention as shown by a number of review articles [1–7]. Systematic research on colloidal semiconductor particles began some 15 to 20 years ago. The initial reason for using colloidal semiconductor sols was to apply these materials as catalysts for free radical and/or redox reactions initiated by light [8, 9]. In these reactions, electrons or positive holes are transferred across the particle-solution interface similar to electrode reactions in electrochemistry. The small particles are, therefore, often referred to as "microelectrodes". In those early days the main aim was to improve the catalytic properties of the semiconductors by simply increasing the surface to volume ratio by decreasing the size of the particles. However, it soon became evident during photocatalysis studies that the particles had certain physico-chemical properties that made the investigation of small particles per se an interesting new field of research.

The use of semiconductors as photo- or photoelectrochemical initiators of vinyl polymerisations has also been described [10–12]. In all these investigations the

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semiconductor was present as a suspension, slurry or as a solid electrode and not as a stable, transparent colloidal sol. This made detailed kinetic investigations of the photopolymerisations impossible. In the first case where polymerisation was induced by the illumination of a transparent semiconductor sol, UV light was necessary because titanium dioxide, with a band gap of 3.2 eV, was used as the semiconductor [13]. In this work the monomer was acrylonitrile and, as polyacrylonitrile is insoluble in its own monomer, the system was also unsuitable to the study of homogeneous polymerisation kinetics. Polymerisation was in fact evidenced by the resulting turbidity of the sol.

Recently, three papers have been published [14–16] describing in detail the photoinitiation of vinyl monomers using colloidal ZnO, TiO_2 and CdS. Also in these investigations it was not possible to study the homogeneous polymerisation kinetics as 2-propanol, in which only the monomers but not the polymers are soluble, was used as the solvent. In fact, in all cases an occlusion and not a bulk or solution polymerisation occurred. The resulting turbidity and co-precipitation of the colloid with the formed polymer implies that no meaningful dependence of polymer yield on monomer or colloid concentration or light intensity could be obtained in these systems.

Until recently colloidal semiconductors were prepared either in aqueous solution or in protic organic solvents in which most common polymers are insoluble. Although colloidal semiconductors have been prepared in organic solvents (17, 18), no report was made about their solubility in methyl methacrylate. Now, due to the recent successful preparation of stable colloidal cadmium sulfide in a wide variety of organic solvents, including methyl methacrylate [19], detailed investigations of the homogeneous polymerisation kinetics of methyl methacrylate photoinitiated by colloidal CdS could be realized [20].

This paper concentrates on the thermal properties of the polymer formed by the photoinitiation of MMA polymerisation using colloidal CdS as the catalyst.

Experimental

Methyl methacrylate (MMA) (Aldrich p.a.) was purified in the usual manner and vacuum distilled immediately before use.

A stock solution of CdS was prepared by injecting, under vigorous stirring, 11 mL H_2S (2×10^{-3} mol L^{-1}) into the gas phase above 250 mL of 1-propanol containing 5×10^{-3} mol L^{-1} 1-(4′-dodecyl)-benzenesulfonic acid (Janssen, 97%, mixture of isomers) and 0.23 g $Cd(ClO_4)_2\cdot6H_2O$ (2.2×10^{-3} mol L^{-1}) (Alfa). Details of the preparation of the colloidal CdS have been described in detail previously [20].

The polymerisation were performed by irradiating 4 mL samples in 1 cm quartz cells with the 435.8 nm line of a 600 W mercury-zenon lamp. The cells were flushed with argon for 15 min to remove dissolved oxygen. Details have been described in detail in a previous paper [20].

After irradiation the formed polymers were precipitated in 100 mL of methanol (Merck, p.a.). The physically entrapped CdS was removed by treatment with 0.5 mol L^{-1} methanolic hydrochloric solution and subsequent washing with methanol until no Cd^{2+} ions could be detected.

For comparison, a PMMA sample was prepared by the bulk polymerisation of MMA at 57°C under a nitrogen atmosphere using 0.5 mol% α,α′-azobisisobutyronitrile (AIBN) as initiator. This polymer was also purified by repeated precipitation of a benzene solution with methanol. A commercial sample of anionically prepared PMMA was obtained from Rohm (FRG).

All polymer samples were dried under vacuum at room temperature for 48 h. The polymer molar masses were determined by gel permeation chromatography (GPC) (Knauer, FRG) using narrow distribution PMMA calibration standards (Rohm, FRG).

Non-isothermal thermogravimetry (TG) and differential TG (DTG) were performed at a heating rate of 10°C min^{-1}, in the temperature range 20–500°C, under a nitrogen flow of 25 cm^3 min^{-1} using a Perkin Elmer TGS-2 instrument. The sample masses were about 5 mg.

Results and discussion

Thermogravimetry was performed on all the PMMA samples prepared using colloidal CdS as the photoinitiator. The shape of both the TG and DTG curves were qualitatively the same independent of the exact polymerisation conditions (i.e. CdS concentration, MMA concentration, light intensity or polymerisation time) so only results concerning one of the samples will be presented here.

The TG curves of the three PMMA samples (CdS, AIBN and anionically initiated) studied are shown in Fig. 1.

PMMA is perhaps one of the most studied polymers in the field of polymer thermal degradation. PMMA thermally degrades almost exclusively by depolymerisation, i.e. monomer is the main product of thermal degradation [21–23]. The kinetics of mass loss are, therefore, determined by the mode of depolymerisation initiation. At first sight, the shape of the TG curve for the CdS initiated PMMA sample resembles that of the anionically prepared PMMA sample, although the curve of the ionic sample is slightly shifted to higher temperatures. The AIBN initiated poly-

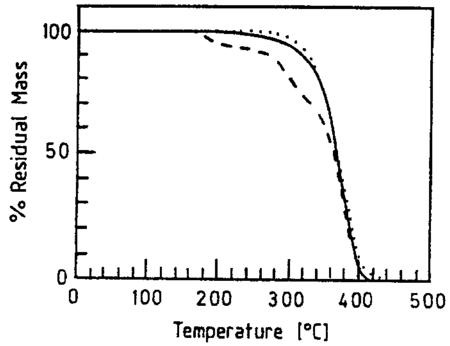


Fig. 1 (a) TG curves of PMMA prepared photochemically using colloidal CdS ($\overline{M}_n$ = 1.3×10^5 g mol^{-1}) (—), free radically using AIBN as the initiator ($\overline{M}_n$ = 0.6×10^5 g mol^{-1}) (- - -) and anionically ($\overline{M}_n$ =0.6×10^5 g mol^{-1}) (·····), heating rate 10 °C min^{-1}, nitrogen flowrate 25 cm^3 min^{-1}

mer is completely different with the commencement of mass loss occurring at considerably lower temperatures and the shape of the TG curve being much more complex, three distinct processes can be observed. It is only by examining the DTG curves that the difference between the anionically and the photochemically initiated PMMA becomes really visible and some similarities between the CdS initiated and the AIBN initiated samples apparent.

The DTG curves of the CdS and AIBN initiated PMMA samples corresponding to the TG curves of Fig. 1 are shown in Fig. 2. The DTG curve of the anionically prepared PMMA sample is not shown in Fig. 2 for the sake of clarity.

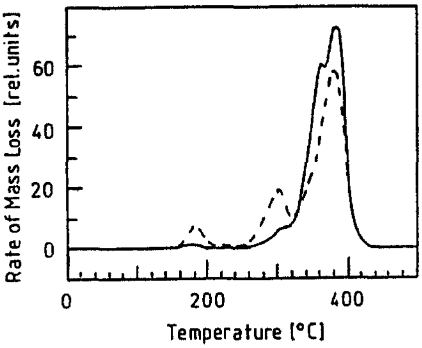


Fig. 2 DTG curves of PMMA prepared photochemically using colloidal CdS (—) and free radically using AIBN as the initiator (- - -), heating rate 10°C min^{-1}, nitrogen flow rate 25 cm^3 min^{-1}, molar masses as in Fig. 1

From Fig. 2 it can be seen that the degradation of the free radically polymerised PMMA occurs in three stages. These stages have been attributed to different modes of initiation of depolymerisation [24–26]. Later, this proposition received experimental confirmation by the examination of the thermal stability of low molar mass model compounds [27] and PMMA samples prepared in the presence of the chain transfer agent *tert*-butyl mercaptan [28]. Thus, the first peak, at 184°C, in the DTG curve of the AIBN initiated PMMA results from thermal depolymerisation initiated by the scission of head-to-head linkages formed during the termination of polymerisation by the combination of two propagating radicals. The second peak, at 300°C, results from scission of the bond β to a terminal double bond which is also formed during polymerisation termination, in this case by disproportionation. The third peak, at 382°C, results from depolymerisation initiated by random main chain scission.

As expected [28], anionically prepared PMMA showed only one peak in the DTG curve, peaking at 383°C (not shown in Fig, 2). Anionically prepared PMMA does not have weak structures resulting from chain termination, i.e. no head-to-head structures and no unsaturated chain end groups. The single DTG peak corresponds to depolymerisation initiated by main chain scission.

When the DTG curve of the PMMA prepared photochemically using colloidal CdS is examined, a very small peak originating from the scission of head to head linkages, as well as a small peak originating from scission of the bond β to a terminal double bond can be seen. This confirms the radical nature of the propagating species in the CdS initiated polymerisation of MMA. Even allowing for the difference in the molar masses of the two samples, these peaks are much smaller than the corresponding peaks in the conventional, radically prepared PMMA sample. However, as well as the two small peaks the photopolymerised sample also has two overlapping peaks at higher temperature and not a single peak corresponding to main chain scission initiated depolymerisation, as is the case with the AIBN initiated PMMA sample.

It is known for PMMA that the areas of the individual peaks are directly proportional to the absolute mass loss resulting from the different initiation modes of depolymerisation. Using a peak separation program, the peaks of the DTG curves were separated and their relative areas calculated, as well as their exact maxima determined. In all cases, the fit of the experimental points was better than 3%. The results of a typical peak separation are shown in Figs 3a and b for the photochemically and AIBN initiated PMMA samples, respectively.

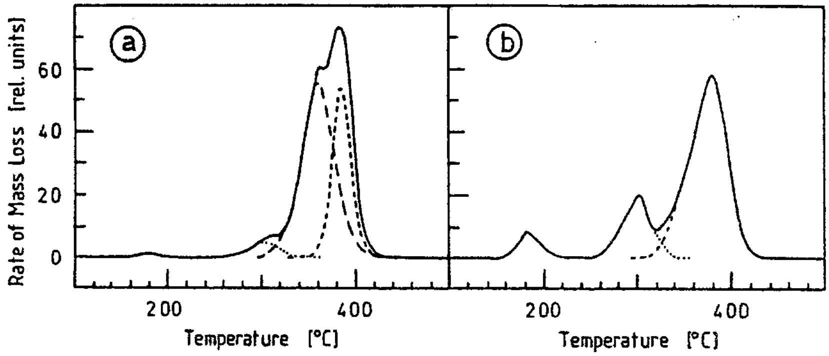


Fig. 3 Deconvolution of the DTG curves of PMMA prepared (a) photochemically using colloidal CdS and (b) free radically using AIBN as the initiator. DTG curve (—), peak 1 (-·-·-), peak 2 (·····), peak 3 (– – –) and peak 4 (- - -). Heating rate 10°C min^{-1}, nitrogen flow rate 25 cm^3 min^{-1}, molar masses as in Fig. 1

The radically prepared PMMA shows three DTG peaks with maxima at 184, 300 and 382°C while the photochemically prepared sample has four DTG peaks at 181, 305, 362, and 388°C. Thus, the three DTG peaks of the radically prepared PMMA correspond to the first, second and fourth peak of the photochemically prepared PMMA, respectively. The new peak at 362°C, present in the DTG curve of the photochemically prepared PMMA, represents a depolymerisation initiation mode via a structure with stability intermediate to that of C–C bonds β to a terminal C–C double bond and that of main chain C–C bonds. The relative peak areas of the three DTG peaks of the AIBN initiated PMMA are 6, 20 and 74% for peaks one to three, respectively. The corresponding values for the four DTG peaks of the photopolymerised PMMA are 1, 4, 62 and 33%, respectively. Thus the new initiation mode is actually the main mode of depolymerisation initiation.

The first thought was that this new peak in the DTG curve of the photopolymerised PMMA might be due to residual cadmium salts in the polymer sample. The

DTG curve of a PMMA sample in which the trapped CdS was left in the polymer, together with the same polymer sample but with the CdS removed by treatment with methanolic HCI, is shown in Fig. 4.

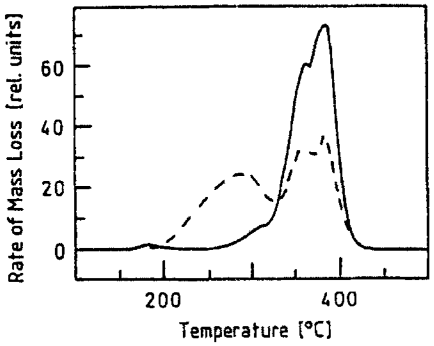
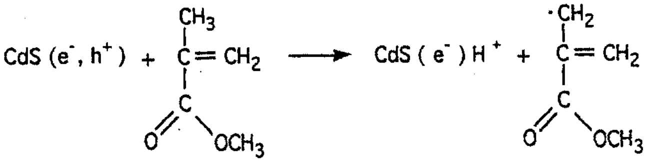


Fig. 4 DTG curves of PMMA prepared photochemically using colloidal CdS before (- - -) and after (—) removal of trapped CdS. Heating rate 10°C $\min^{-1}$, nitrogen flow rate 25 $cm^3 \min^{-1}$, molar mass of both samples $\overline{M}_n = 1.3\times10^5$ g mol^{-1}

Figure 4 proves conclusively that the new peak in the DTG curve of CdS initiated PMMA is not the result of the polymer containing trapped CdS as the presence of the semiconductor actually causes a decrease in the stability of the PMMA and not the observed increase. Also, after the initial low temperature mass loss, the polymer remaining still shows the presence of the new DTG peak.

We propose that the new peak in the DTG curve of PMMA photopolymerised using colloidal CdS is also the result of depolymerisation initiated by the scission of the bond in the β-position to chain end unsaturation but that the vinyl group does not arise during chain termination but during the polymerisation initiation process. Thus, the positive hole, formed in the valence band of the semiconductor when an electon is excited to the conduction band upon absorption of a quantum of light, oxidises a methyl methacrylate molecule by abstraction of a hydrogen atom. The hydrogen atom fills the positive hole and results in a MMA radical:



$$\mathrm{CdS}(e^-,h^+) + CH_2{=}C(CH_3)COOCH_3 \longrightarrow \mathrm{CdS}(e^-)H^+ + CH_2{=}C(\cdot CH_2)COOCH_3$$

The MMA radical reacts with another methyl methacrylate molecule to give the propagating radical. Addition to the methylene side of the double bond of the MMA molecule is more likely than addition to the substituted end for steric reasons and because the resulting radical, as in normal free radical polymerisations, is less stable when the radical is on the methylene carbon. This means that every polymer molecule commences with an unsaturated chain end. The difference between this chain end unsaturation and the unsaturation arising from chain termination by disproportionation is that the bond in the β-position is a CH_2–CH_2 bond and not a

CH_2–CR_2. It is to be expected that the unsubstituted bond would be thermally more stable than the substituted one and so depolymerisation initiated by β-scission would result in a DTG peak between that of the peak resulting from normal chain end initiated depolymerisation and main chain scission initiated depolymerisation.

The two small, low temperature peaks visible in the DTG curve of the CdS initiated PMMA are smaller than the corresponding peaks in the AIBN initiated sample. This is a consequence of extensive chain transfer to $CdS(e^-)H^+$, the excited, reduced semiconductor particle formed during polymerisation initiation, occurring. This reduces the amount of radical-radical chain termination and so reduces the magnitude of the DTG peaks originating from the weak structures introduced into the polymer chains in this manner.

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