

Polymerization Studies: The Application of Differential Thermogravimetric Analysis

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SYNOPSIS

The application of differential thermogravimetric analysis (DTGA) to the study of polymerization mechanisms is illustrated using as examples the radical polymerization of di-*n*-alkyl itaconates and methyl methacrylate (MMA). Five poly(di-*n*-alkyl itaconates) were prepared in bulk, both in the presence and absence of *n*-dodecyl mercaptan and in solution using AIBN as initiator. The poly(methyl methacrylate) (PMMA) was photoinitiated using colloidal CdS as a photosensitizer. The thermal properties of the resulting polymers are described in terms of the proposed polymerization mechanisms. The advantages and disadvantages of DTGA for the identification of thermally weak structures are discussed.

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INTRODUCTION

The polymerization, as well as the nonoxidative thermal stability of poly(methyl methacrylate) (PMMA) have been the subject of many investigations. It has been established, e.g., by thermal volatilization analysis,¹ that PMMA thermally decomposes by depolymerization. Generally, the depolymerization of PMMA can be initiated by the scission of head-to-head bonds, at unsaturated chain ends and by main chain scission. Consequently, three differential thermogravimetric (DTG) maxima are registered in the case of PMMA prepared by free-radical polymerization.² Grassie and Vance³ first discussed the possibility of determining the relative amounts of thermally weak structures from the amounts of PMMA depolymerized at different temperatures and the possibility of changing these amounts by altering the polymerization conditions. They also demonstrated that the effect of chain

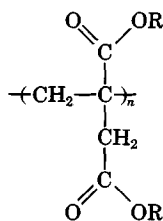
transfer in the polymerization of MMA can be established by studying the thermal properties of the formed polymer. By using low molar mass model compounds, Cacioli et al.⁴ conclusively proved the origin of the three maxima observed in the DTG curve of radically prepared PMMA. Also, Kashiwagi et al.² showed that the first two DTG maxima, ascribed to depolymerization initiated by the scission of head-to-head bonds and bonds in the β position to chain-end unsaturation, can be decreased or completely suppressed when PMMA is synthesized in the presence of the chain-transfer agent *tert*-butyl mercaptan. PMMA synthesized by anionic polymerization has been shown to be thermally more stable than PMMA obtained by free-radical polymerization due to the absence of chain-end unsaturation and head-to-head structures.⁵ In this case, only one DTG maximum is observed.

Poly(di-*n*-alkyl itaconates) also predominantly thermally degrade by depolymerization,⁶⁻⁸ which should allow the application of thermogravimetric analysis (TGA) to the study of the polymerization mechanisms of these polymers. Five poly(di-*n*-alkyl itaconates), which are vinylidene type polymers of the following structure:

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Table I Di-*n*-alkyl Itaconate Bulk Polymerization at 60°C in the Presence of DDM; $c(\text{AIBN}) = 0.5 \text{ mol } \%$

Sample	$c(\text{DDM})$ (mmol/L)	Yield (%)	\bar{M}_w (g/mol) (GPC)
PDMI-D0	0	11.7	7.34×10^4
PDMI-D1	90	4.8	9.07×10^3
PDMI-D2	149	1.7	7.48×10^3
PDEI-D0	0	1.0	5.83×10^4
PDEI-D1	73	0.5	2.36×10^4
PDEI-D2	122	0.5	—
PDHI-D0	0	8.0	1.29×10^5
PDHI-D1	23	5.1	1.62×10^4
PDHI-D2	45	4.4	1.00×10^4
PDHI-D3	63	3.6	7.37×10^3
PDHI-D4	80	2.2	6.51×10^3
PDHI-D5	100	2.3	5.06×10^3
PDHI-D6	150	2.1	4.23×10^3
PDOI-D0	0	12.1	1.04×10^5
PDOI-D1	22	5.6	1.38×10^4
PDOI-D2	88	5.3	5.19×10^3



where R is a methyl, ethyl, *n*-butyl, *n*-hexyl, or *n*-octyl group and PMMA, prepared using colloidal

cadmium sulfide as a photoinitiator, were investigated. The use of the novel initiator, colloidal CdS, results in a chain-end structure, the thermal stability of which has only recently been described.⁹

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.). The crude products were vacuum-distilled before use. Dimethyl itaconate (DMI) (Aldrich, p.a.) was recrystallized from methanol. Benzene (Alkaloid, p.a.), toluene, dioxan, and chloroform (all Merck p.a.) were distilled before use.

For all polymerizations, α, α' -azobisisobutyronitrile (AIBN) was used as the initiator. The bulk polymerizations, both in the presence and absence of the chain-transfer agent *n*-dodecyl mercaptan (DDM), were performed in sealed glass ampules under high vacuum at 60°C. Details of the bulk polymerizations are given in Table I.

Two samples of poly(di-*n*-hexyl itaconate) (PDHI) were prepared in bulk at 40 and 70°C using 0.1 and 2.0 mol % AIBN, respectively, to obtain a very high and a very low molar mass sample, respectively, without the interference of DDM.

The solution polymerizations were performed under a nitrogen flow at 57°C. Details of the polymerizations of di-*n*-alkyl itaconates in benzene are given in Table II, whereas those of DBI polymerized in toluene, chloroform, and dioxan are shown in Table III.

Table II Conditions for the Polymerization of Di-*n*-alkyl Itaconates in Benzene at 57°C under Nitrogen

Sample	Concn of Monomer (mol/L)	Concn of Benzene (mol/L)	Concn of AIBN (mmol/L)	Yield (%)	\bar{M}_w (g/mol)
PDMI-B0	6.12	0.00	394	6.7	2.67×10^4
PDMI-B1	1.90	8.10	38	2.6	1.66×10^4
PDMI-B2	0.95	10.29	10	4.4	8.42×10^3
PDBI-B0	3.99	0.00	120	11.5	1.09×10^5
PDBI-B1	2.48	4.32	46	13.4	3.63×10^4
PDBI-B2	1.24	7.79	12	2.9	1.77×10^4
PDBI-B3	0.62	9.53	3	3.4	3.36×10^3
PDHI-B0	3.24	0.00	209	8.6	5.34×10^4
PDHI-B1	2.01	3.95	81	4.9	1.51×10^4
PDHI-B2	1.01	7.61	20	4.3	8.31×10^3

Table III Conditions for the Polymerization of Di-*n*-butyl Itaconate in Various Solvents at 57°C under Nitrogen

Sample	Solvent	Concn of Monomer (mol/L)	Concn of Solvent (mol/L)	Concn of AIBN (mmol/L)	Yield (%)	\bar{M}_w (g/mol)
PDBI	None	3.99	0.00	120	11.5	10.9×10^4
PDBI-T1	Toluene	1.24	6.51	12	4.4	2.58×10^4
PDBI-T2	Toluene	0.62	7.97	3	1.6	1.29×10^4
PDBI-D1	Dioxan	2.48	4.46	46	11.4	3.32×10^4
PDBI-D2	Dioxan	1.24	8.17	12	6.4	1.86×10^4
PDBI-D3	Dioxan	0.64	9.86	3	2.2	8.99×10^3
PDBI-C3	Chloroform	1.81	6.68	25	7.6	1.62×10^4

The bulk polymerizations were taken to yields of not more than 20%, whereas the polymerizations performed in the presence of a chain-transfer agent or in solution were taken to yields not exceeding about 5 and 10%, respectively. The polymers were precipitated using a large excess of methanol containing 5% water and purified by repeated precipitation from benzene solutions using methanol.

Colloidal cadmium sulfide was prepared by the injection of H₂S gas to a solution of cadmium perchlorate in 1-propanol containing 1-(4'-dodecyl)benzenesulfonic acid (Janssen, 97% mixture of isomers) as a stabilizer. Details of the preparation have been given elsewhere.^{9,10} The 1-propanol was removed under vacuum at 35°C and the resulting powder redispersed in MMA. The colloidal solution was purged with argon for 15 min to remove oxygen. Polymerization was initiated by irradiating with the 435.8 nm line of a 600 W mercury-xenon lamp for 60 min. The yield of polymer was about 5%. The polymer was precipitated in a large excess of methanol. The physically entrapped CdS was removed by treatment with dilute methanolic hydrochloric acid before the polymer was purified by repeated precipitation from benzolic solution using methanol.

The molar masses of the polymers were determined by GPC (Knauer/Trilab) using PMMA samples (Röhm GmbH, Germany) as standards (Tables I-III). 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. Nonisothermal experiments were performed in the temperature range 30–500°C at heating rates of 2.5 and 10°/min. The average sample size was 5 mg and the nitrogen flowrate 25 cm³/min.

RESULTS AND DISCUSSION

Poly(di-*n*-alkyl itaconates)

The volatile products of the nonoxidative thermolysis of poly(di-*n*-alkyl itaconates) consist of approximately 90% monomer and of compounds mostly resulting from side-chain scission (such as alkyl alcohol, alkyl acetate, etc.).^{7,11} Under the same thermolysis conditions, the composition of the volatile products does not depend on the size of the ester substituent in the investigated range from the dimethyl to the di-*n*-octyl derivative. On the other hand, the shapes of the DTG curves of poly(di-*n*-alkyl itaconates) change with increasing ester substituent size (Fig. 1). The dimethyl and diethyl derivatives are characterized by a single peak with a shoulder that becomes a plateau in the case of poly(di-*n*-butyl itaconate) (PDBI). Two distinct peaks are registered in the case of the di-*n*-hexyl and di-*n*-octyl derivatives. The relative magnitudes, i.e., the shapes, of the DTG peaks do not depend on the molar mass of the polymers.

Based on the temperatures of the characteristic DTG maxima of PMMA and the structural similarity of PMMA and poly(di-*n*-alkyl itaconates), the first DTG maximum of poly(di-*n*-alkyl itaconates) was assumed to originate from the depolymerization of chain-end unsaturated polymer molecules and the second maximum to main-chain scission initiation of depolymerization. Head-to-head structures appear not to be formed in poly(di-*n*-alkyl itaconates). They would result in a DTG peak at lower temperatures than of 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.

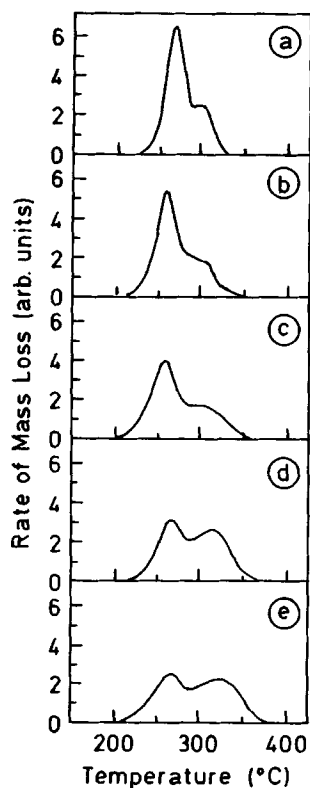


Figure 1 DTG curves of (a) PDMI, (b) PDEI, (c) PDBI, (d) PDHI, and (e) PDOI, prepared in bulk at 40°C using 0.5 mol % AIBN as initiator. Heating rate 2.5°/min.

The origin of the first DTG maximum was confirmed by synthesizing PDHI in the presence of DDM. This transfer agent suppresses chain termination by radical-radical reactions by reacting with the growing polymer radical. The change in the content of chain-end double bonds of PDHI samples prepared in the presence of various amounts of DDM 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 is proportional to the intensity (height) of the peak at 1640 cm^{-1} multiplied by the number-average molar mass of the sample. Correspondingly, with increasing mercaptan concentration, the relative number of double bonds per polymer chain and the size of the first DTG maximum both decrease (Fig. 2).

That the changed shape of the DTG curves of PDHI samples prepared in the presence of DDM was not a molar mass effect was confirmed by the unchanged shape of the DTG curves of PDHI sam-

ples of greatly differing molar masses but prepared in the absence of DDM.⁸

As indicated by the minor degradation products (alkyl acetates, alkyl acrylates CO_2 , CO , etc.),^{7,11} depolymerization is also, to a small extent, initiated over the whole mass loss range by side-chain scission. This initiation reaction is not registered as a separate DTG maximum. As the first DTG maximum is not completely suppressed in the case of PDHI synthesized in the presence of larger amounts of DDM ($>2 \times 10^{-2}\text{ mol/dm}^3$) (Fig. 2), it may be assumed that a broad flat peak, usually covered by the other two DTG maxima, could originate from the side-chain scission initiation of depolymerization. Using a peak separation program, the DTG curves of PDHI samples prepared with concentrations of DDM ranging between 60 and 150 mmol/L could only be satisfactorily split into their constituent peaks when a broad peak covering the whole mass loss was assumed.

The first DTG peak of PDMI, PDEI, PDBI, and PDOI also decreased in magnitude with increasing DDM concentration, although the effect with PDMI was not so pronounced as with the other polymers (Fig. 3). The fact that the first peak in the DTG curve of PDMI is almost unaffected by the addition of DDM suggests that this peak does not arise from thermally weak structures originating from termination by disproportionation.

Theoretically, in the case of a polymer that completely thermally depolymerizes and that preferentially terminates by disproportionation during free-radical polymerization, two DTG maxima of similar

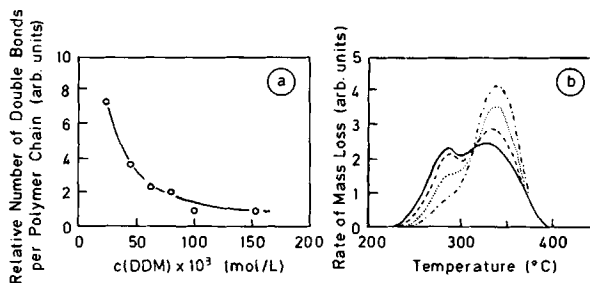


Figure 2 (a) Dependence of the relative number of chain-end double bonds on the amount of DDM present during the bulk polymerization of DHL. (b) DTG curves of PDHI prepared in the presence of (—) 0, (---) 23, (·····) 63, and (-·-·-) 150 mmol/L DDM. Heating rate 10°/min. Polymerization conditions given in Table I.

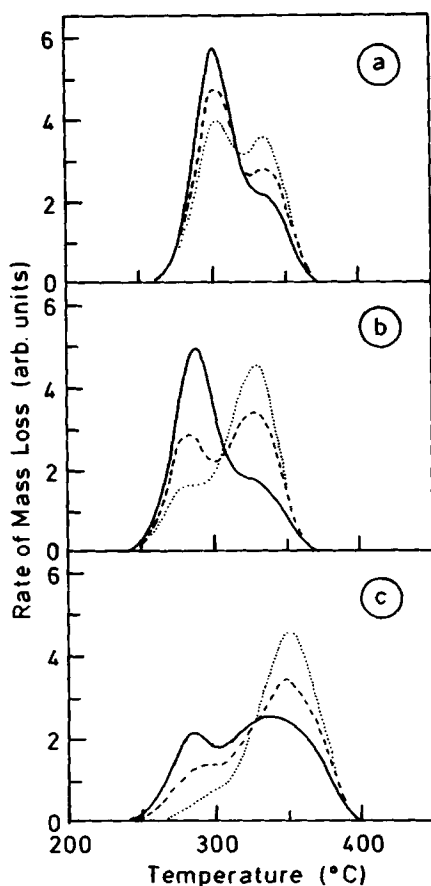
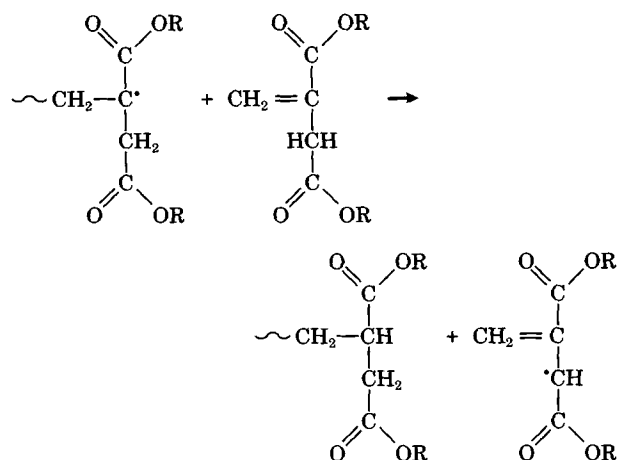


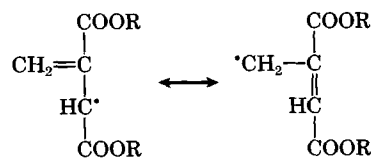
Figure 3 DTG curves of (a) PDMI, (b) PDEI, and (c) PDOI prepared in the presence of DDM. Concentrations of DDM in mmol/L: (a) (—) 0, (---) 90, (·····) 149; (b) (—) 0, (---) 73, (·····) 122; (c) (—) 0, (---) 22, (·····) 88. Polymerization conditions given in Table I. Heating rate $10^\circ/\text{min}$.

size, originating from the two different depolymerization initiation modes, should be registered if the depolymerization dezip length is long enough. In the case of a short dezip length, the peak arising from main-chain scission initiation of depolymerization should increase in magnitude relative to the peak arising from chain-end initiation of depolymerization. The first DTG maximum of the lower poly (di-*n*-alkyl itaconates) is, however, considerably larger than the second one, implying an additional source of end-chain unsaturation.

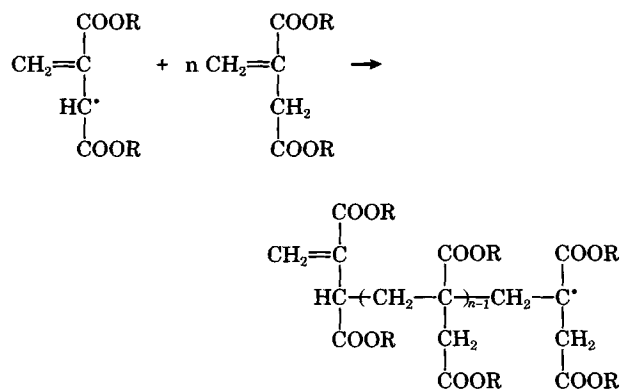
Nagai and Yoshida¹² suggested that, due to the allylic structure of the monomer, the affinity toward chain transfer to monomer should be considerable in the case of the itaconates. Such chain transfer would involve the abstraction of an allylic hydrogen to terminate the growth of the chain:



The resulting radical is resonance-stabilized:



This radical can then reinitiate the growth of a new polymer chain that will have an unsaturated chain end:



Differential thermogravimetric analysis (DTGA) supports this hypothesis, the relatively large initial DTG peak originating from the reinitiation of polymerization after chain transfer has occurred. With increasing ester substituent size, the affinity toward chain transfer to monomer during free radical polymerization is assumed to decrease due to steric reasons,¹² thus, the decrease in the size of the first DTG maximum with increasing substituent size

(Fig. 1) and the reduced effect of DDM in decreasing the size of the first DTG peak in PDMI.

The complete absence of a peak corresponding to head-to-head groups supports the assumption that radical-radical polymerization termination, both by combination and disproportionation, is almost completely, if not entirely, suppressed during the polymerization of these monomers.

A series of PDBI samples was synthesized in benzene, which was chosen as the solvent because of its supposed very low chain-transfer activity. The DTG curves of these polymers are shown in Figure 4. The first DTG maximum decreases with increasing benzene concentration. This change was the first indication that chain transfer to benzene might be unexpectedly high in the polymerization of di-*n*-alkyl itaconates. This behavior was confirmed for the case of DBI where a chain transfer to a benzene constant of 1.89×10^{-3} was obtained at 57°C. This compares to a value of 0.158×10^{-5} for *n*-butyl methacrylate at 60°C.¹³

Similar DTG curves and effects (Fig. 5), 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.¹⁴ These results will be discussed in more detail in a forthcoming publication.

Series of the other poly(di-*n*-alkyl itaconates) were also prepared in benzene solution. The results of the DTGA are shown in Figure 6. The effect of the benzene on the DTG curves of PDMI is, as with the DDM series, less pronounced than with the other

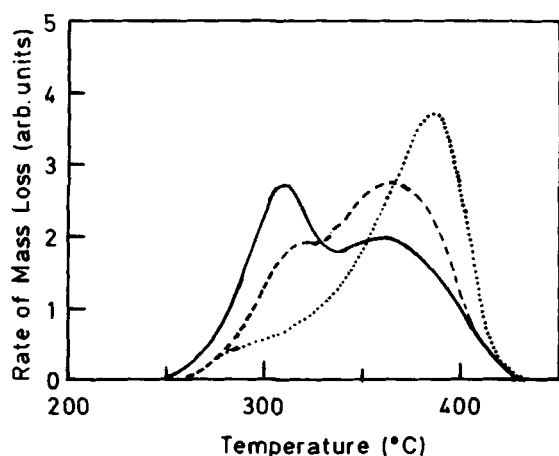


Figure 4 DTG curves of PDBI samples prepared in benzene solution. Concentrations of benzene in mol/L: (—) 0; (---) 7.78; (·····) 9.53. Polymerization conditions given in Table II. Heating rate 10°/min.

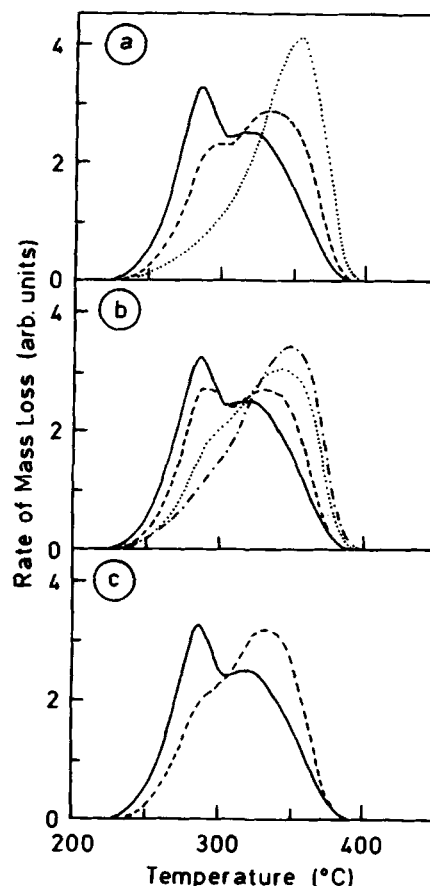


Figure 5 DTG curves of PDBI prepared in the presence of (a) toluene, (b) dioxan, and (c) chloroform. Concentration of solvent in mol/L: (a) (—) 0, (---) 6.51, (·····) 7.97; (b) (—) 0, (---) 4.46, (·····) 8.17, (-·-·-) 9.86; (c) (—) 0, (---) 6.68. Heating rate 10°/min.

poly(di-*n*-alkyl itaconates). This behavior suggests that in this case the transfer constant to monomer is so high that, combined with the high concentration of monomer, transfer to monomer overrides the effects of chain transfer to any other species.

PMMA Prepared Using Colloidal CdS as a Photoinitiator

The initiation of the polymerization of MMA using colloidal CdS has recently been described.⁹ This is a heterogeneous system in which the photogenerated positive hole in the valence band of the semiconductor is assumed to initiate polymerization. The DTG curve of the PMMA sample prepared using colloidal CdS as a photoinitiator ($\bar{M}_n = 1.3 \times 10^5$ g/mol) is shown in Figure 7(a) together with a free

radically prepared sample of comparable molar mass ($\bar{M}_n = 0.6 \times 10^5$ g/mol). The first two small DTG peaks confirm the radical mechanism of polymerization.

Using a peak separation program, the DTG curve of the PMMA sample prepared using colloidal CdS was separated into its constituent peaks [Fig. 7(b)]. The first obvious comment to be made is that an additional peak, representing a previously unreported depolymerization initiation mode, is present when this new photoinitiator is used and that this new initiation mode is actually the main mode of initiation of depolymerization. It must represent the scission of a bond intermediate in strength between a bond β to a terminal unsaturated group, formed during polymerization as the result of chain termination by disproportionation and a main-chain bond.

It is proposed that this new depolymerization initiation mode also originates from the scission of a bond in the β position to a terminal unsaturated group, but in this case, the β bond is a tail-to-tail bond originating during the initiation of polymerization by the CdS. Thus, photogenerated positive holes in CdS particles oxidize MMA molecules by abstracting hydrogen atoms. The electron of the abstracted hydrogen atom fills the positive charge, leaving a proton on the surface of the CdS particle:

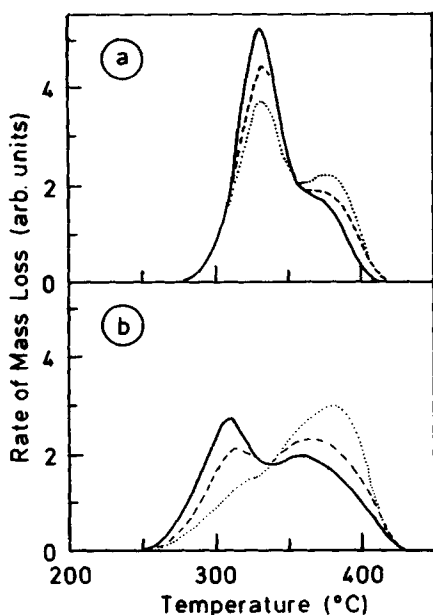


Figure 6 DTG curves of (a) PDMI and (b) PDHI prepared in benzene solution. Concentration of benzene in mol/L: (a) (—) 0, (---) 8.10, (· · · · ·) 10.29; (b) (—) 0, (---) 3.95, (· · · · ·) 7.61. Polymerization conditions given in Table II. Heating rate $10^\circ/\text{min}$.

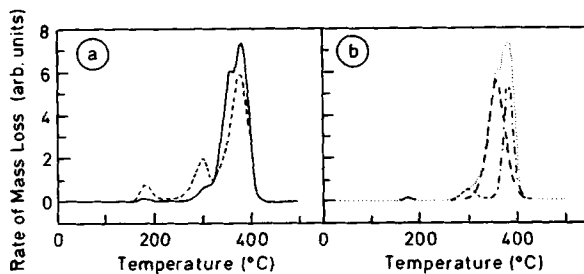
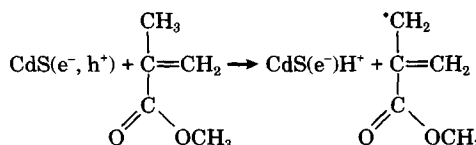
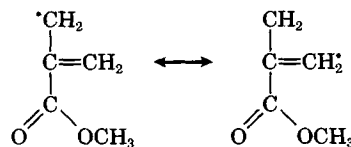


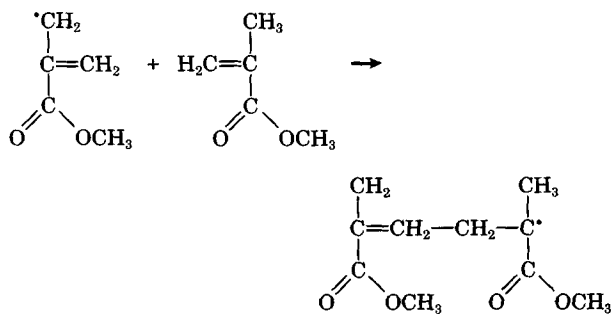
Figure 7 (a) DTG curves of PMMA prepared using (—) colloidal CdS and (---) AIBN as initiators. Heating rate $10^\circ/\text{min}$. (b) Separation of the CdS-initiated PMMA DTG curve into its constituent peaks.



The resulting MMA radical is resonance-stabilized, implying that abstraction of a hydrogen atom from the methylene group results in an equivalent radical:



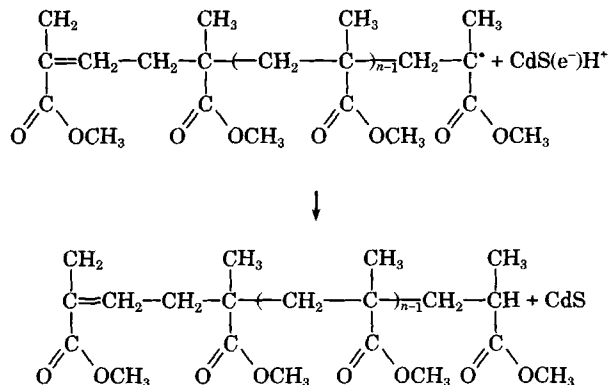
This resonance-stabilized radical then reacts with an MMA molecule to form the propagating radical:



For steric and stability reasons, it is most likely that the resonance-stabilized radical reacts at the methylene side of the MMA molecule. Propagation then proceeds normally.

Chain termination must predominantly occur by chain transfer to cadmium sulfide particles as the first and second peaks in the DTG curve [Fig. 7(a)]

are much smaller than in normal radically prepared PMMA. It has been shown kinetically that the chain transfer must actually occur to a cadmium sulfide particle carrying a proton, i.e., $\text{CdS}(e^-)\text{H}^+$, generated in the initiation step⁹:



It should be noted that this mechanism entails that every polymer chain, in the absence of chain transfer to monomer or polymer, commences with an unsaturated group and that the bond in the β position to the terminal unsaturation is a tail-to-tail bond. A tail-to-tail structure in the β position would be expected to be intermediate in strength to a head-to-tail structure in the β position and main-chain bonds. Because of the very small size of the first and second DTG peaks, normal radical-radical termination, either by combination or disproportionation, must not occur to any appreciable extent and the chain transfer to CdS particles must be very high. In fact, an apparent chain-transfer constant to molecular CdS of 1.4 was determined.⁹

Thus, using the information gained from DTGA it was possible to propose a polymerization mechanism for this new initiation system that explains the small size of the first and second DTG peaks and the existence of a depolymerization initiation mode not usually present in the thermal degradation of radically prepared PMMA.

CONCLUSIONS

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

DTGA could be more commonly used in the analysis of thermally weak structures in polymers that predominantly depolymerize. Whereas in the analytical techniques of FTIR and high-resolution NMR the thermally weak structures are measured directly, in DTGA, the effects of the weak structures are magnified as they initiate chain reactions, the effects of which are registered. The detection limit for DTGA is, therefore, lower than those of FTIR and NMR. Also, no special purification of the polymers is required for DTGA, whereas for FTIR and NMR, the polymer samples must be rigorously purified from monomer and other impurities that could affect the very small signals obtained using these techniques. The disadvantage of DTGA is that some prior knowledge of the thermal degradation mechanism is required.

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