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THERMAL BEHAVIOUR OF GLYCIDYL METHACRYLATE HOMOPOLYMERS AND COPOLYMERS

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Abstract

The paper describes the effect of molecular mass and copolymer composition on thermal behaviour of homopolymers and copolymers of glycidyl methacrylate and methyl methacrylate. The polymerisation was done by using group transfer polymerization (GTP) and free radical techniques. A multistep decomposition was observed in polymers prepared by free radical technique indicating the presence of weak linkages in the backbone. Copolymers prepared by GTP had fewer weak sites and degraded in single step by a random chain scission.

Keywords: group transfer polymerisation, H–H linkage, molecular mass, random chain scission, weak linkages

Introduction

Glycidyl methacrylate (GMA)-based homopolymers and its copolymers with methyl methacrylate (MMA) have received considerable attention owing to their versatile applications [1]. It is, therefore, of interest to study the thermal degradation behaviour of these polymers. Studies on thermal stability of poly(glycidyl methacrylate) (PGMA) and poly(glycidyl methacrylate-co-methyl methacrylate) (PGMA-co-PMMA) having molecular masses in the range of 200,000 to 366,000 and with GMA content varying between 11.5 to 89.3 mol% have been reported [2, 3]. The thermal degradation of PGMA was found to occur in two main steps with rate maxima at 313 and 380°C and yields monomer as the predominant volatile product (44–60%). The monomers were also the major products of degradation in the case PGMA-co-PMMA. However, cyclized products were also observed.

The present paper reports the results of the studies on thermal behaviour of PGMA and PGMA-co-PMMA prepared by group transfer polymerization (GTP) and free radical techniques. The objective of the work was to study the effect of molecular mass and molecular mass distribution (MWD) on the thermal behaviour of PGMA and PGMA-co-PMMA.

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Experimental

Materials

[(1-Methoxy-2-methyl-1-propenyl)oxy]trimethylsilane (MTS) (Aldrich) was distilled over CaH_2 (*b.p.* 35°C l5 mm^{-1} Hg). Tetrahydrofuran (THF) (S.D Fine Chemicals, Bombay) was purified by refluxing over fresh sodium benzophenone complex. It was further distilled over oligo-poly(styryl) lithium under reduced pressure immediately before use. Methyl methacrylate (MMA) (Gujarat State Fertiliser Corp., Baroda) was passed through an activated alumina (G-87) column to remove inhibitor, stirred over CaH_2 for 8 h vacuum distilled at 10^{-3} mm Hg, and stored under nitrogen at 0°C. Just prior to polymerization it was treated with triisobutyl aluminium (TIBAL), until a persistent yellowish color was observed and redistilled under reduced pressure (10^{-3} mm Hg) [4]. GMA (Fluka) was passed through an activated alumina column, stirred over CaH_2 and distilled under reduced pressure. Just prior to use GMA was treated with poly(styryl)lithium till a persistent reddish brown color was observed. It was then fractionally distilled under reduced pressure (*b.p.* 45°C 3 mm^{-1} Hg) [1]. Tetrabutylammonium bibenzoate (TBABB) (*m.p.* 102°C) was prepared according to the literature procedure [5] and dried under vacuum before use.

PGMA and PGMA-co-PMMA by GTP

PGMA and PGMA-co-PMMA were synthesized by GTP technique using MTS as an initiator and TBABB as catalyst in THF at 0°C [6]. Under these conditions no ring opening of the epoxide was observed as confirmed by the ^{1}H-NMR spectra of (co)polymers. The composition, molecular mass and MWD data for the synthesised polymers are shown in Table l .

Table 1 Composition, $\overline{M}_n$, intrinsic viscosity, $\overline{M}_v$, and polydispersity of PGMA and PGMA-co-PMMA prepared by GTP

Sample code	GMA in copolymer[a]/mol%	$\overline{M}_n$ (GPC)[b]	$M_w/\overline{M}_n$ (GPC)[b]	Intrinsic viscosity/mL g^{-1}	$\overline{M}_v$
PGMA-T1	100	6100	1.26	9.5	6870
PGMA-T2	100	15400	1.53	23.0	21345
PGMA-T3	100	30400	1.37	39.0	42000
MG-T21	21	19000	1.15	25.0	23750
MG-T45	45	13000	1.26	32.5	33250
MG-T51	51	13700	1.26	24.5	23150
MG-T74	74	17800	1.40	20.7	18650

[a] using ^{1}H-NMR

[b] by GPC using PMMA calibration standard

PGMA and PGMA-co-PMMA by radical polymerization

A mixture of MMA and GMA of the desired composition and carbon tetrachloride (1 mL) as the chain transfer agent were placed in a three-necked flask. Nitrogen was bubbled through the solution and benzoyl peroxide (3 mol% based on monomer) was added. The reaction mixture was stirred under nitrogen at 80°C till an appreciable viscosity was observed. The mixture was diluted with chloroform and then precipitated into excess methanol. The polymers were dried at 50°C for 24 h under reduced pressure. The composition, intrinsic viscosity and viscosity average molecular mass data for the synthesized polymers are given in Table 2.

Table 2 Composition, intrinsic viscosity and $\overline{M}_v$ of PGMA-co-PMMA prepared by free radical polymerization

Sample code	GMA in copolymer[a]/mol%	Intrinsic viscosity/mL g^{-1}	$\overline{M}_v$
PGMA-R	100	17.6	32000
MG-R75	25	8.4	13000
MG-R51	49	23	45220
MG-R31	69	17.6	32000

[a] using ^{1}H-NMR

Characterization

A Bruker 200 MHz NMR spectrometer was used for recording ^{1}H-NMR spectra of polymers. The solvent used was $CDCl_3$ (30°C, concentration 4 mg mL^{-1}) with tetramethylsilane as an internal standard. The molecular mass and MWD for the polymers (0.3% w/v in THF) were determined using Waters gel permeation chromatograph model GPC/ALC 150C equipped with a refractive index detector. The measurements were carried out using Waters μ-Styragel columns at a temperature of 30°C. THF was used as eluent at a flow rate of 2 mL min^{-1}. PMMA of known molecular mass was used as standard. Thermogravimetric (TG) studies were carried out on a DuPont 2100 thermal analyzer having a 951 TG module under nitrogen atmosphere at a heating rate of 10°C min^{-1}. A sample mass of 12 ± 2 mg was used.

Results and discussion

Typical TG traces of polymers are given in Fig. 1. For assessing relative thermal stability of polymers with different molecular masses the TG trace was characterized by determining (a) onset temperature of decomposition (T_{onset}), (b) temperature of maximum rate of mass loss (T_{peak}) (obtained from derivative thermogravimetric trace) and (c) final decomposition temperature (T_f). In samples where multistep decomposition was observed each step was characterized by determining the above mentioned parameters as well as the mass loss.

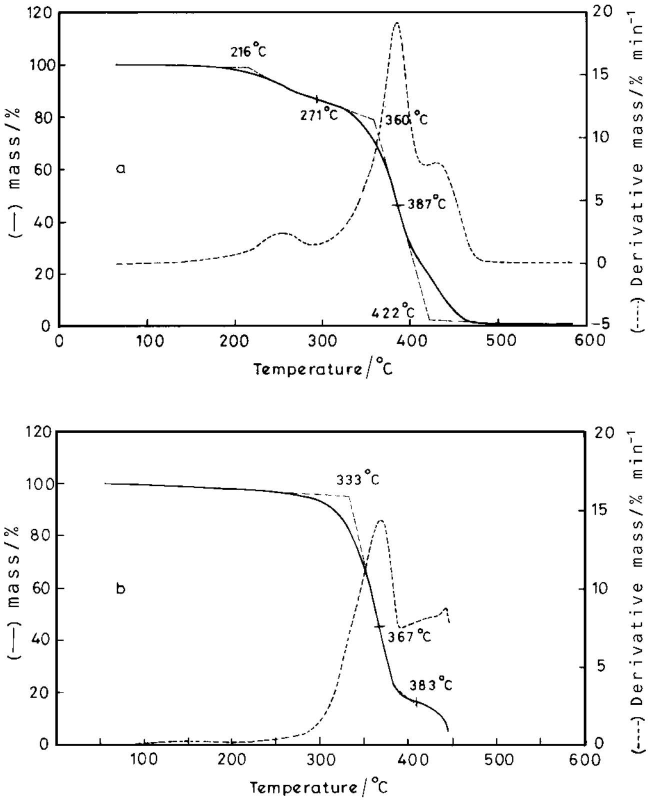

Fig. 1 TG traces of poly(glycidyl methacrylate) in N_2 atmosphere; a – PGMA-T1 and b – PGMA-T2

The TG data on PGMA and PGMA-co-PMMA prepared by GTP is given in Table 3. Both low molecular mass PGMA (M_n=6100) (PGMA-T1) and high molecular mass PGMA (M_n=30400) (PGMA-T3) prepared by GTP showed mass loss below 250°C. Such a behaviour has been observed in PMMA and was attributed to the presence of H–H linkages in the polymer backbone. Recent studies have indicated that, in PMMA prepared by GTP H–H units affect the degradation of polymer [7]. Two other degradation steps with rate maxima at about 380 and 430°C were also observed in these polymer samples. These can be associated with end group initiated degradation at lower temperature followed by random chain scission of the polymer backbone at higher temperature. PGMA of intermediate molecular mass (M_n=15400) (PGMA-T2) exhibits a single step degradation which can be attributed to random chain scission.

The copolymer rich in MMA (79 mol% MMA) prepared by GTP (Fig. 2) shows a single step degradation above 250°C. This can be attributed to chain end initiated depolymerisation of MMA sequence. As the GMA content is increased from 45 to 51 mol%, the thermal behaviour of the copolymers prepared by GTP shows slight

Table 3 TG studies on PGMA and PGMA-co-PMMA prepared by GTP

Sample code	Mass loss/ <250°C	T_{onset}/°C	T_{peak}/°C	Final decomposition temperature/°C	Mass loss/%
PGMA-T1	–	142	261	288	12
		292	386	419	70
		422	430	477	16
PGMA-T2	–	230	369	395	77.5
PGMA-T3	–	130	–	260	7.3
		283	373	413	78
		441	427	487	11.8
MG-T21	7.3	297	396	453	92.5
MG-T45	–	284	389	455	99.0
MG-T51	7.0	284	384	492	91.0
MG-T74	4.5	298	381	419	80.0
		419	–	472	13.6

resemblance to GMA homopolymer of comparable molecular mass. In the intermediate range of molecular masses (M_n=13000), there is no mass loss in the region below 250°C. A single step degradation above 280°C is observed which can be attributed to random chain scission. The high molecular mass copolymer shows a mass loss in the region below 250°C followed by a two-step degradation due to end group initiation and random chain scission. The copolymer containing 74 mol% GMA behaves in a similar fashion. Since the molecular mass is relatively high (M_n=17800) it exhibits a mass loss below 250°C as well as two step degradation above 250°C which can be attributed to end group initiation followed by random chain scission.

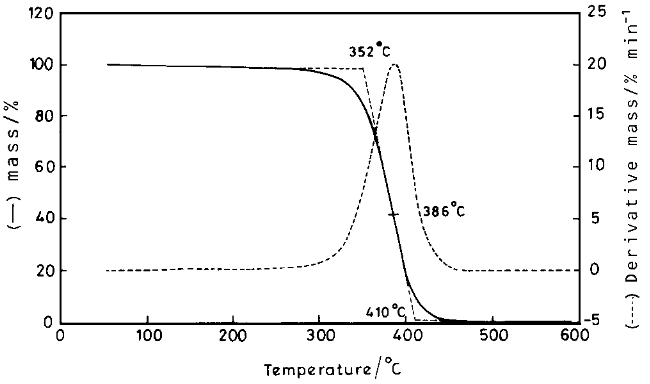

Fig. 2 TG trace of copolymer MG-T21

Table 4 TG studies on PGMA and PGMA-co-PMMA prepared by free radical polymerization

Sample code	T_{onset}/°C	T_{peak}/°C	Final decomposition temperature/°C	Mass loss/%
PGMA-R	165	–	259	6.4
	261	306	327	23.0
	327	361	408	54.5
	408	427	480	10.5
MG-R75	167	192	224	11.8
	242	303	335	31.8
	335	369	408	38.2
MG-R51	117	181	219	13.6
	227	300	332	31.8
	332	363	392	27.3
	392	424	495	22.7
MG-R31	134	211	232	10.0
	233	311	332	30.0
	333	361	400	35.5
	400	430	490	20.8

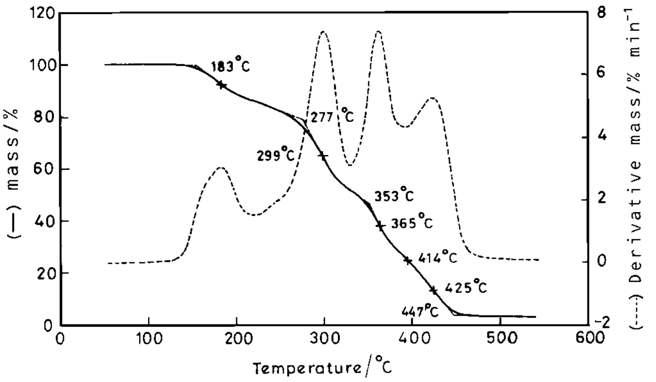

Fig. 3 TG trace of MG-R51

The results of TG analysis of PGMA and PGMA-co-PMMA prepared by free radical polymerization are given in Table 4. Olefinic end group initiated degradation and random chain scission are also observed in free radically prepared PGMA. However in this case there is an extra step involved between end group initiation and random chain scission (Fig. 3). This degradation step has a rate maxima at 361°C and can be attributed to –CCl_3 end groups which are introduced as a result of free radical polymerization in presence of CCl_4 and may constitute weak sites in the polymer chain. The copolymers prepared by free radical polymerization degrade in four steps which can be attributed to a – H–H linkages, b – olefinic end group initiation, c – –CCl_3 end groups and d – random chain scission.

Conclusions

PGMA and PGMA-co-PMMA obtained by GTP degraded in a single step. About 7% mass loss was observed below 250°C which can be attributed to presence of H–H linkages in the polymers. Free radically prepared PGMA and PGMA-co-PMMA, on the other hand, degraded in four steps which can be attributed to initiation at weak linkages (i.e. H–H linkages, unsaturation and presence of –CCl_3 group at chain ends) and random chain scission.

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