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THERMAL CHARACTERIZATION OF METHYL METHACRYLATE–ALKYL METHACRYLATE COPOLYMERS

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ABSTRACT

Several copolymers of methyl methacrylate (MMA) with lauryl methacrylate (LMA) or cetyl methacrylate (CMA) were prepared in bulk at 70 ° C using 1% benzoyl peroxide as initiator. The copolymer compositions were determined by ^{1}H nuclear magnetic resonance (NMR) spectroscopy from the peak areas at $\delta = 3.59$ ppm (due to $-OCH_3$ protons of MMA) and at $\delta = 3.93$ ppm (due to $-OCH_2-$ protons of LMA and CMA). The monomer reactivity ratios were found to be $r_1 = 0.25$ and $r_2 = 0.63$ for MMA (M_1) and LMA copolymers and $r_1 = 0.65$ and $r_2 = 0.71$ for MMA and CMA copolymers. A multistep degradation of copolymers was indicated by DSC and TG studies. Degradation in the temperature range 200–300 ° C was influenced by the copolymer composition. An increase in the MMA content of the copolymer resulted in a decrease in weight loss in this region. Total loss in weight was observed around 400 ° C. Pyrolysis gas chromatographic studies of homopolymers indicated a loss of monomer during the pyrolysis of polymer.

INTRODUCTION

The thermal degradation of poly(methyl methacrylate) (PMMA) and its copolymers has been extensively investigated in the past. The sole product of degradation of PMMA is monomer, which is produced by a reverse polymerization (depolymerization) reaction. The zip length of this radical chain process is large (of the order of 10^3), so that chains of sufficiently low degree of polymerization unzip completely once initiated by scission [1]. However, the degradation of PMMA is very much dependent on the mode of polymerization and the presence of comonomer units in the backbone [2]. For example when PMMA prepared by free radical polymerization is subjected to a programmed rate of heating it undergoes depolymerization in two stages [3]. The first stage of degradation is due to initiation at unsaturated chain ends, and occurs below 300 ° C. The second stage of degradation observed at high temperature is due to initiation by random scission of the

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backbone. One step degradation is observed in PMMA prepared by anionic polymerization.

The degradation behaviour of copolymers of MMA depends largely on the nature of the comonomers [4]. If the comonomer is another methacrylate, which also undergoes depolymerization, then unzipping will continue to produce MMA and the corresponding monomer. This behaviour has been demonstrated in alkyl methacrylates with linear ester side groups (ethyl and *n*-propyl methacrylate). However, in copolymers of *n*-butyl methacrylate with butene-1 monomer carbon monoxide and methane are also obtained [5,6]. Monomers are the sole product of degradation up to a temperature of 400 °C in copolymers of MMA and iso-octyl or iso-decyl methacrylate [7].

The thermal behaviour of copolymers of MMA with alkyl methacrylates based on linear alcohols of more than ten carbon atoms has not been reported in the literature. Such investigations are very useful not only for the understanding of the mechanism of degradation,, but because they can offer a means of copolymer characterization using thermal techniques. Therefore this study, which deals with the synthesis, characterization and thermal behaviour of copolymers of MMA with lauryl methacrylate (LMA) or cetyl methacrylate (CMA), was undertaken.

EXPERIMENTAL

The lauryl methacrylate and cetyl methacrylate monomers were prepared by transesterification reaction using methyl methacrylate and lauryl alcohol or cetyl alcohol in the presence of sulphuric acid as catalyst [7]. Copolymerization of MMA with LMA or CMA was carried out in the bulk at 70 °C using 1% benzoyl peroxide as initiator. Four different monomer ratios were used in the initial feed, and the reaction was carried out for 50–120 min so as to keep conversion below 15%. The structural determination of the copolymers was carried out by recording the ^{1}H nuclear magnetic resonance (NMR) spectra using a Jeol JNM-FX 100 FT–NMR spectrophotometer and tetramethylsilane as an internal standard.

The thermal behaviour of the copolymer samples in air was evaluated using a Du Pont 1090 thermal analyser with a 951 TG module. A heating rate of 10 °C min^{-1} was used and polymer samples of 10 ± 2 mg were employed. The thermogravimetric traces obtained were characterized by determining the decomposition temperatures, i.e. the final decomposition temperature FDT and the temperature at the maximum rate of weight loss T_{max}. Some DSC traces of a few polymer samples were also recorded in static air using a Du Pont 9900 thermal analyser with a 910 DSC module. A heating rate of 10 °C min^{-1} was used and the sample size was 11 ± 2 mg.

In order to determine the products of degradation, a pyrolysis gas chromatographic technique (Py–GC) was employed. A Perkin–Elmer Sigma

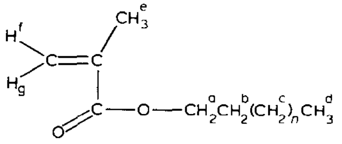
300 gas chromatograph attached to a Perkin–Elmer Sigma 3600 recorder was used for this purpose. A non-polar column (length, 8 ft) packed with 5% silica gel SE 300 and a hydrogen–air flame ionization detector were used. The temperatures of both the injector block and the detector were kept at 280 °C. The column was heated at a heating rate of 3 °C min^{-1} from 70 °C to 280 °C. The flow rate of the carrier gas (argon) was 25 ml min^{-1}. The pyrolysis probe was heated to 400 °C at a rate of 10 °C μs^{-1} for 5 s.

RESULTS AND DISCUSSION

Preparation and characterization

Monomers

The overall yields of LMA and CMA from the transesterification reaction were in the range 70%–75%. The monomers were characterized by recording their ^{1}H NMR spectra. In these monomers seven sets of equivalent protons are present which resonate at different field strengths due to their different environments. The methyl protons (d) of the alkyl side chain appear at $\delta = 0.879$ ppm (triplet, 3H) and the methylene protons (c) appear at 1.262 ppm (singlet, 18 H in LMA and 26 in CMA). A singlet is observed at 1.66 ppm (2H) and can be attributed to the methylene group at position (b) of the side chain. The proton resonance signal observed at 1.936 ppm (3H) is due to the allylic protons (e) (i.e. the methyl group).



The OCH_2 appears as a triplet centred at 4.132 ppm (a). The two olefinic protons are magnetically inequivalent and are observed at 5.52 ppm (triplet, 1H) and 6.093 ppm (singlet, 1H).

Polymers

The details of the compositions of the copolymers together with their designations are given in Table 1. These polymer designations are used throughout this paper.

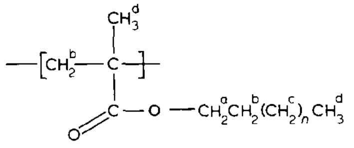
The homopolymers and copolymers are sticky in nature. The presence of long alkyl side chains in these polymers forces the main chain apart, thereby increasing the free volume and reducing the T_g value to below room temperature. The polymers are therefore in a rubbery state at room temperature.

TABLE 1

Copolymerization of MMA with lauryl methacrylate (LMA) and cetyl methacrylate (CMA)

Monomer M_2	Sample designation	Mole fraction of MMA in feed	Conversion (%)	Mole fraction of MMA in polymer
LMA	PLMA	–	15.2	–
	LM_1	0.125	16.4	0.160
	LM_2	0.250	16.5	0.273
	LM_3	0.500	16.7	0.333
	LM_4	0.751	8.8	0.591
CMA	PCMA	–	8.5	–
	CM_1	0.125	6.9	0.142
	CM_2	0.250	6.8	0.301
	CM_3	0.500	11.6	0.309
	CM_4	0.751	11.3	0.700

The percentage conversion was kept to a low value in the copolymerization reaction ($<20\%$). The structural characterization of the homopolymers and copolymers was carried out using NMR spectroscopy. The structure of the polymers and their proton types can be depicted as follows



where $n = 9$ in PLMA and 13 in PCMA.

In these polymers four sets of equivalent protons are present. The methylene protons (a) resonate at a low field due to their proximity to the electronegative oxygen atom. The methylene protons (b) and (c) resonate at high field but over a narrow range because their environments are only slightly different. The methyl protons (d) appear at high fields. The chemical shifts in the homopolymers of MMA and LMA are shown in Table 2. The spectra of the copolymers show the combined features of both homopolymers. A slight paramagnetic shift occurs in the resonance peaks of the copolymers as can be seen from the chemical shifts of the protons in the homopolymers and copolymers. Typical NMR spectra of the copolymers of MMA and LMA are given in Figs. 1 and 2. The two hydrogens of the OCH_2 group present in LMA produce a singlet around 3.93 ppm, whereas the OCH_3 group in PMMA produces a signal at 3.59 ppm. Quantitative NMR analysis can, therefore, be used to determine the copolymer composition. The method provides a more accurate and rapid determination of copolymer composition in comparison with conventional techniques. The calculation of

TABLE 2

Chemical shifts of protons in PMMA and PLMA

Polymer	Proton type	Group	Number of protons	(ppm)
PMMA	a	$-OC\underline{H}_3$	3	3.59
	b	$-C\underline{H}_2$ (of backbone)	2	1.82
	d	$-C\underline{H}_3$(α-methyl)	3	0.87–1.02
PLMA	a	$-C\underline{H}_2-$	2	3.93
	b	$-OCH_2C\underline{H}-$	2	1.94
	c	$-OCH_2CH_2(C\underline{H}_2)_n-$	18	1.28
	d	$-C\underline{H}_3$	3	0.89

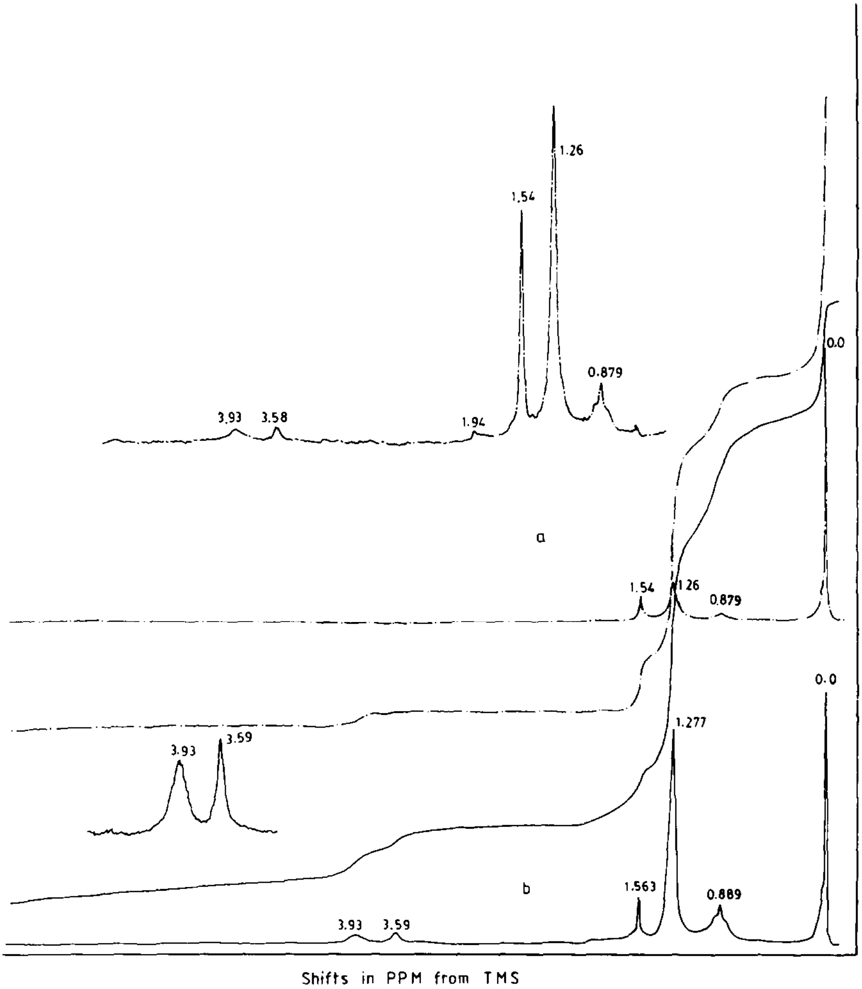


Fig. 1. ^{1}H NMR spectra of copolymers: (a) LM_2 and (b) LM_3.

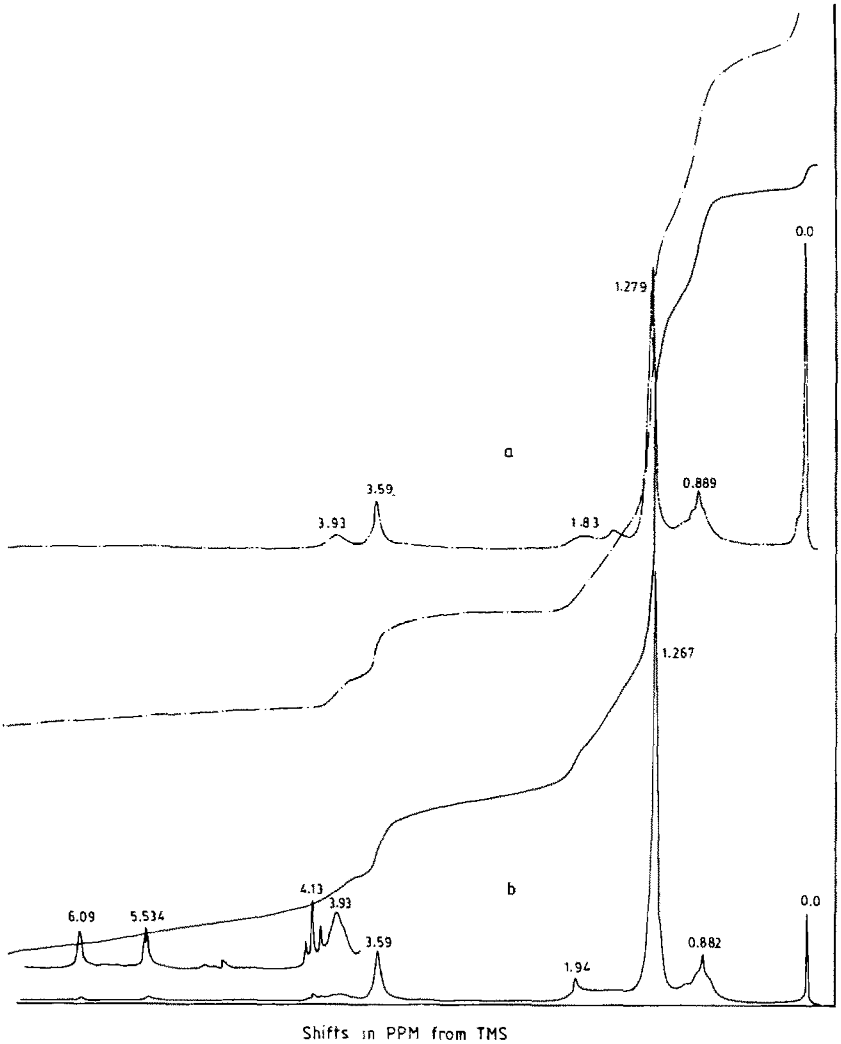


Fig. 2. ^{1}H NMR spectra of copolymers: (a) LM_4 and (b) CM_4.

techniques. The calculation of copolymer composition is based on the fact that the area under a resonance peak, as measured by integration, is directly proportional to the number of protons producing the signal. It is obvious from Figs. 1 and 2 that as the mole fraction of LMA increases in the initial feed, an increase in the area of the peak at 3.93 ppm occurs. In this study, the molar ratios of the monomers in the copolymers were calculated from the ratios of the peak areas at 3.59 ppm (corresponding to 3H of PMMA) and 3.93 ppm (corresponding to 2H of LMA or CMA).

The copolymers of CMA and MMA, as well as PCMA, were contaminated with some unreacted monomer (Fig. 2). This was indicated by the appearance of a triplet centred at $\delta = 4.13$ ppm and also by the peaks at

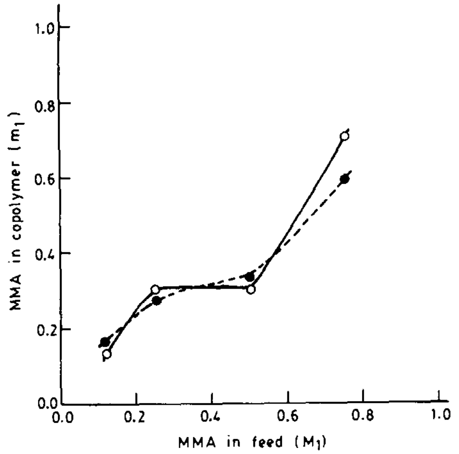


Fig. 3. Effect of mole fraction of MMA in the feed on copolymer composition: (●----●) MMA–LMA copolymers, (○———○) MMA–CMA copolymers.

$\delta = 5.52$ ppm and 6.09 ppm. These copolymers were prepared by bulk polymerization and subsequent precipitation in methanol. Since the monomer was sparingly soluble in methanol it was also precipitated. Repeated washing of the copolymers with methanol was not adequate to remove the traces of monomer adsorbed on the copolymers. The copolymer compositions were determined by integrating the peaks at 3.59 ppm (due to 3H of the $-OCH_3$ group of MMA) and 3.93 ppm (due to 2H of the $-OCH_2$ group of CMA), taking into account the contributions due to monomer. The copolymer compositions thus determined are given in Table 1. A plot of mole fraction of MMA in the feed vs. the mole fraction in the copolymers is given in Fig. 3.

Determination of monomer reactivity ratios

The monomer reactivity ratios were determined for the copolymerization of MMA (r_1) with LMA or CMA (r_2) by graphical [8] (Fig. 4), Kelen–Tudos [9] (Fig. 5) and Joshi–Joshi [10] methods. Good agreement between the r_1 and r_2 values calculated using the different methods is observed (Table 3). The random nature of the copolymers is indicated from the monomer reactivity ratios.

Thermal behaviour

In order to investigate the effect of comonomer (i.e. MMA) on the thermal stabilities of poly(lauryl methacrylate) (PLMA) and poly(cetyl methacrylate) (PCMA), differential scanning calorimetric and thermogravimetric studies were carried out.

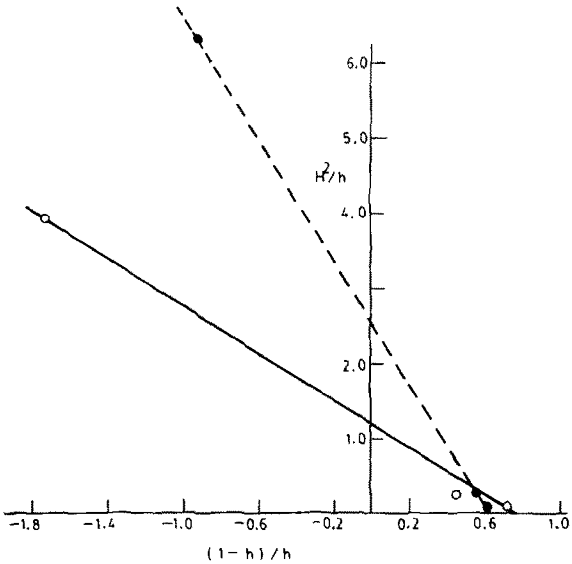


Fig. 4. Determination of monomer reactivity ratios by graphical method: (●----●) MMA–LMA copolymers, (○———○) MMA–CMA copolymers.

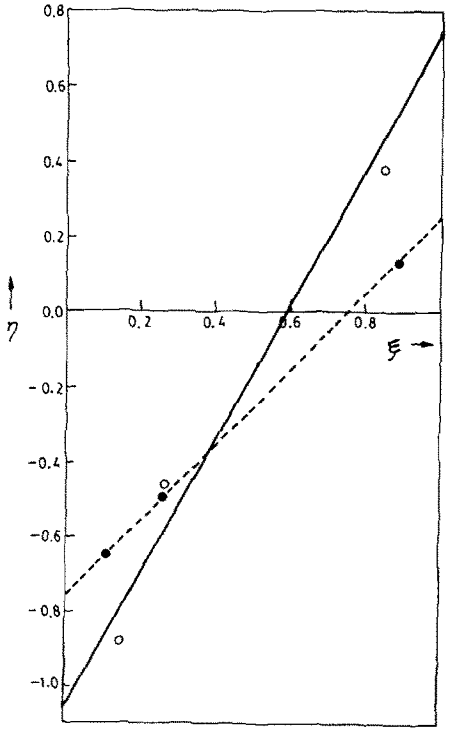


Fig. 5. Determination of monomer reactivity ratios by Kelen and Tudos method: (●----●) MMA–LMA copolymers, (○———○) MMA–CMA copolymers.

TABLE 3

Monomer reactivity ratios of methyl methacrylate (M_1) and lauryl and cetyl methacrylate (M_2)

Method	Monomers			
	MMA (r_1)	LMA (r_2)	MMA (r_1)	CMA (r_2)
Graphical	0.25	0.63	0.62	0.74
Kelen–Tudos	0.26	0.63	0.75	0.74
Joshi–Joshi	0.25	0.63	0.64	0.71
Average value	0.25	0.63	0.67	0.73

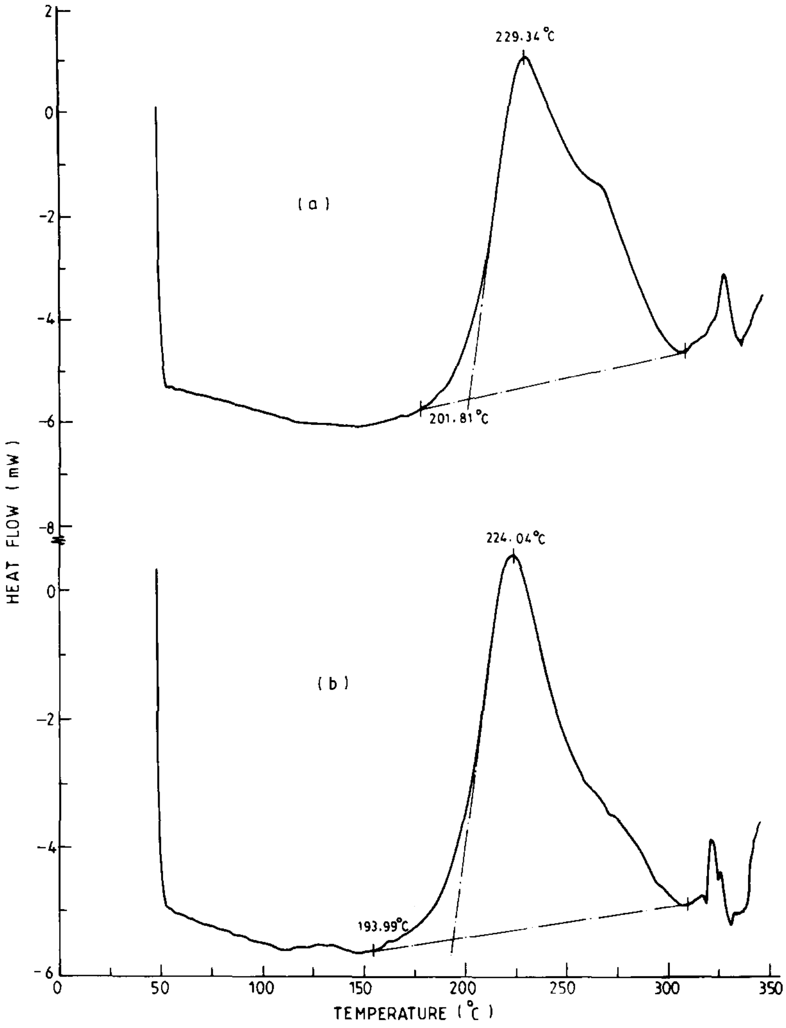


Fig. 6. DSC curves of: (a) CM_1; (b) CM_3.

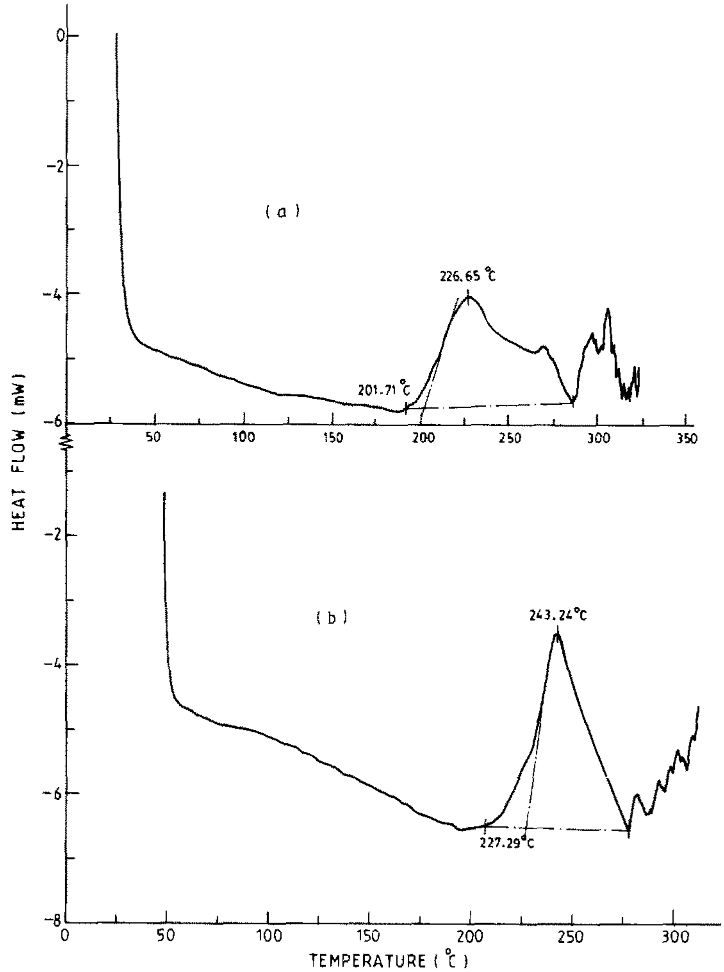


Fig. 7. DSC curves of; (a) CM_4; (b) LM_4.

DSC traces of copolymer samples recorded in the temperature range 50–350 °C are given in Figs. 6 and 7. In all these samples more than one exothermic transition is observed in this temperature range. The first exotherm is observed in the temperature range 200–300 °C. The second exotherm appears at higher temperatures. The exothermic transition can be characterized be determining the following parameters: (a) the temperature at which deviation from the baseline is observed (onset of exotherm (T_1')); (b) the extrapolated onset of the exotherm (T_1); (c) the temperature of peak position (T_{exo}); (d) the temperature of completion of the exotherm (T_f); (e) the heat of reaction (from the area under the exothermic transition).

This data is summarized in Table 4. Increases in T_1', T_1 and T_{exo} are observed on introduction of MMA to PLMA, but no systematic trend is observed in PCMA copolymers. T_{exo} remains almost constant in PCMA and

TABLE 4

Results of DSC scans of various polymers and copolymers

Sample	T_i' (°C)	T_i (°C)	T_{exo} (°C)	T_f (°C)	Heat of reaction (J g^{-1})
PLMA	193.3	207.4	234.5	307.5	145.50
LM$_1$	220.0	230.2	243.8	296.7	74.76
LM$_4$	207.5	227.3	243.2	278.3	57.26
PCMA	179.8	206.7	228.0	311.5	153.20
CM$_1$	177.5	201.8	229.3	308.3	209.30
CM$_3$	155.0	194.0	224.0	310.0	192.60
CM$_4$	191.3	201.7	226.6	286.6	42.33

its copolymers. The heat of reaction is higher in homopolymers and is decreased by the presence of MMA in the backbone. From these observations it can be concluded that the first degradation step in the polymers is primarily due to the breakdown of PLMA or PCMA, and the degradation of MMA does not occur at this temperature. Our earlier studies have indicated that PMMA starts to degrade only around 295 °C.

The TG traces of the polymer samples were recorded in air in the temperature range 40–500 °C (Fig. 8). The FDT and T_{max} values can be obtained from the TG traces. The weight loss curves show a number of kinetically different steps. For all such steps the T_{max} values are noted (T_{max-1}, T_{max-2}, T_{max-3}, etc.). The weight losses at these peak positions are also noted. The final temperature for each step is taken as the valley point on the rate of weight loss vs. temperature plot. The weight loss at this temperature is also recorded. All these data are summarized in Table 5. The copolymer samples start to lose weight above 200 °C and the T_{max} values appear at temperatures close to the T_{exo} values of the DSC scans. The temperature of the maximum weight loss is observed at a higher temperature and it shows a decreasing trend with increase in MMA content. For the PLMA–MMA system the shoulder at 298 °C becomes more noticeable with an increase in MMA content. In copolymers of CMA–MMA no such shoulder is observed in the DTG trace when low mole fractions of MMA are present. However, in sample CM$_4$ such a shoulder is observed at 290 °C. Weak sites present in PMMA are believed to be responsible for the onset of degradation around 300 °C. It thus appears that the shoulder observed at 294 ± 4 °C is due to the breakdown of MMA segments in the copolymers. The degradation of the copolymers becomes complicated by the presence of higher concentrations of MMA in the backbone and multiple decomposition steps are observed in the DTG traces.

The pyrolysis gas chromatograms of PLMA and PCMA show only one peak with retention times of 31.29 and 43.88 min respectively. This indicates

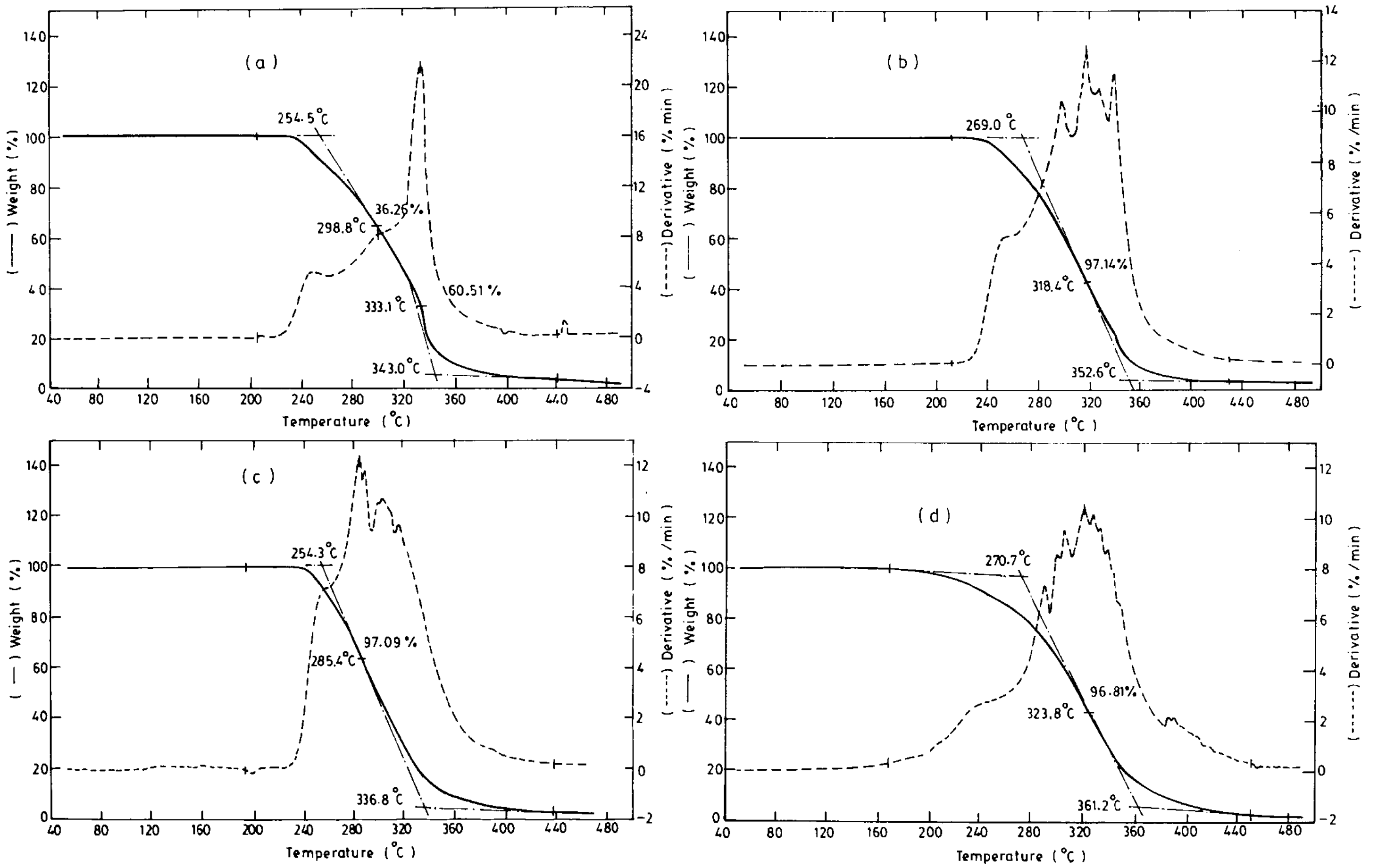


Fig. 8. TG curves of copolymers: (a) LM_1; (b) LM_3; (c) LM_4; (d) CM_4.

TABLE 5

Results of TG studies of various polymers and copolymers

Samples	T_{max-1} (°C)	FDT (°C)	T_{max-2} (°C)	T_{max-3} (°C)	T_{max-4} (°C)	T_{max-5} (°C)	FDT (°C)
PLMA	246	258	320	–	–	–	341
	(13)	(18)	(39.5)	(–)	(–)	(–)	(89.3)
LM_1	246	264	298	331.1	–	–	343
	(6)	(15)	(36.2)	(60.5)	(–)	(–)	(97)
LM_3	255	263	298	318.4	326	340	352.6
	(8)	(12)	(38)	(42)	(67)	(78)	(97.1)
LM_4	256	260	283	298	303	316	336.6
	(11)	(14)	(33)	(50)	(54)	(67)	(97.1)
PCMA	242	253	335	–	–	–	410
	(9)	(11)	(43)	(–)	(–)	(–)	(97)
CM_1	244	255	336	–	–	–	394
	(9)	(13)	(54)	(–)	(–)	(–)	(98.8)
CM_4	240	252	290	306	320	323	361.2
	(9)	(12)	(28)	(40)	(53)	(57)	(96.8)

Values given in parentheses show the total weight loss up to those temperatures.

the formation of a single species during the degradation of the polymers at 400 °C. The retention times of the volatile products (monomers) are significantly different in PLMA and PCMA. Therefore, Py–GC can be used to identify the monomers present in copolymers of poly(alkyl methacrylates).

On the basis of the above studies it can be concluded that copolymers of MMA with LMA or CMA prepared by free radical polymerization are random in nature. The thermal degradation of poly(cetyl methacrylate) and poly(lauryl methacrylate) proceeds predominantly by the loss of the monomer (depolymerization).

REFERENCES

1 N. Grassie and H.W. Melville, Proc. R. Soc. London, Ser. A, 199 (1949) 1.
2 I.C. McNeil, Eur. Polym. J., 4 (1968) 21.
3 I.C. McNeil, Eur. Polym. J., 6 (1970) 373.
4 I.C. McNeil, in N. Grassie (Ed.), Developments in Polymer Degradation, Vol. 7, Elsevier Applied Science, Barking, 1986, p. 22.
5 I.C. McNeil, in N. Grassie (Ed.), Developments in Polymer Degradation, Vol. 1, Elsevier Applied Science, Barking, 1977, p. 43.
6 A. Guyot, M. Bert, A. Michel and I.C. McNeil, Eur. Polym. J., 7 (1971) 471.
7 I.K. Varma, M. Varma Nair and V.K. Karan, unpublished results.
8 E.A. Collins, J. Bares and F.W. Billmeyer, Experiments in Polymer Science, 1st edn., Wiley, New York, 1973, p. 20.
9 T. Kelen and F. Tudos, J. Macromol. Sci. Chem., 9 (1975) 1.
10 M.R. Joshi and S.G. Joshi, J. Macromol. Sci., 25 (1971) 1329.