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THERMAL BEHAVIOUR OF COPOLYMERS OF METHYL METHACRYLATE AND ISO-OCTYL/ISO-DECYL METHACRYLATE

I. K. Varma, M. V. Nair and *V. K. Karan*

CENTER FOR MATERIALS SCIENCE AND TECHNOLOGY
INDIAN INSTITUTE OF TECHNOLOGY, DELHI, HAUZ KHAS,
NEW DELHI 110016, INDIA

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Thermal behaviour of copolymers of methyl methacrylate (MMA) with iso-octyliso-decyl methacrylate was investigated using dynamic thermogravimetry, mass spectroscopy and pyrolysis gas chromatography. The copolymer samples were stable upto 250 °C. Total loss in weight was observed around 400 °C. The degradation in homopolymers as well as copolymers proceeded by predominant loss of monomer.

Copolymers of methyl methacrylate with several vinyl monomers have been investigated in the past. These copolymers are widely used in the field of plastics, paints, automotive coatings, surgery and medicine [1, 2] and as viscosity index improvers for lubricating oils [3, 4]. We have earlier reported the copolymerisation of HEMA with alkyl acrylates and alkyl methacrylates [5–8].

Viscosity index improvers based on polymethacrylates are being used extensively in lubricating oils. Such polymers are generally synthesised by copolymerisation of monomer mixtures of methacrylic acid ester with C_1–C_{30} alcohols. Characterisation of such a multicomponent system is a bit difficult. Thermal analytical techniques have been widely used in polymer characterisation. It would therefore, be of interest to study thermal behaviour of multicomponent polymethacrylates having long alkyl side chains. In the present paper we report the copolymerisation of MMA with iso-octyl methacrylate (OMA) and iso-decyl methacrylate (DMA) using benzoyl peroxide as an initiator. The characterisation of copolymers was done by using ir ^{1}H &^{13}C–NMR, intrinsic viscosity determination, and dynamic thermogravimetry. The products of pyrolysis of homopolymers and copolymers were investigated by mass spectroscopy and pyrolysis gas chromatography.

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Experimental

Preparation of OMA and DMA

These monomers were prepared by transesterification of methyl methacrylate (AR grade) with iso-octyl alcohol/iso-decyl alcohol in presence of sulphuric acid as a catalyst. For this purpose 0.3 mole MMA having hydroquinone as an inhibitor (0.68 g) was placed in a soxhlet apparatus and 0.1 mole of iso-octyl or iso-decyl alcohol, 150 mL of benzene and 1.2 mL conc. H_2SO_4 were added. In order to absorb methanol produced during transesterification reaction, molecular sieves of 4 Å were placed in the soxhlet thimble. The solution was refluxed for 12 h and then cooled and washed with water (3 × 10 mL) to remove sulphuric acid. It was then dried over anhydrous sodium sulphate. Alkyl methacrylates were separated from various constituents by fractional distillation and purified by distillation under reduced pressure. The overall yield of alkyl methacrylate was around 70%.

Polymerization

The monomers were freed from the inhibitor by washing several times with 10% solution of sodium hydroxide till the aqueous layer was free from colour. The monomer was then washed with distilled water and then dried over anhydrous Na_2SO_4 and distilled.

A known quantity of the monomer/monomers was placed in a three necked flask fitted with a water condenser and an inlet tube for passing nitrogen. Whole assembly was placed in an oil bath maintained at 70°. Dry nitrogen was passed through the flask for 10 min and then 1% benzoyl peroxide (*w*/*w*) was added and the reaction was carried out for 35–60 min, so as to keep the percentage conversion below 12%. The solution was then slowly poured in about 100 mL of methanol with continuous stirring. The precipitated polymer was isolated, washed with methanol and dried in a vacuum oven at 80–90° for 24 h.

Characterisation of polymers

Molecular characterisation of homopolymers and copolymers was done by intrinsic viscosity measurements using chloroform as solvent at 25 ± 1°. The polymer concentration was varied from 0.3–1 g/dL and an Ubbelhode viscometer was used for viscosity determinations.

A Nicolet 5D–X FT–IR spectrophotometer was used for recording the spectra of copolymer samples in thin films cast from chloroform solution.

Proton NMR spectra of polymer samples were recorded in $CDCl_3$ using a Jeol FT–NMR (JNM–FX 100) spectrophotometer and tetramethyl silane as an internal standard. ^{13}C–NMR were also recorded in $CDCl_3$.

Thermal stability of the polymer samples in air atmosphere was evaluated by DuPont 1090 thermal analyser having a 951 TG module and using 10 ± 2 mg of polymer sample at a heating rate of 10 deg/min. From the thermogravimetric traces, initial decomposition temperature (IDT), final decomposition temperature (FDT) were determined by extrapolation. Temperature of maximum rate of weight loss (T_{max}), was determined from the differential thermogravimetric traces.

A Jeol JMS DX 300 mass spectrophotometer having TMS–200 data processing system was used for recording the mass spectra. Copolymer samples were pyrolysed on the ion probe at 250° and the volatile products were analysed.

A Perkin–Elmer Sigma 300 gas chromatograph attached to the Perkin–Elmer sigma 3600 recorder was used for pyrolysis gas chromatography (Py–GC) studies. A non-polar 8′ long column packed with 5% silica gel SE–30 was used. Hydrogen air flame ionisation detector (FID) was used to identify the retention times for the fractions. Argon was the carrier gas. Temperature of both injector block and detector was kept at 280°. The column was heated at a heating rate of 3 deg/min from 70°–280°. Rate of flow of the carrier gas was 25 ml/min. Pyrolysis probe was heated to 400° at a rate of 10 °C/μsec for 5 seconds.

Results and discussion

Several copolymers samples were prepared by varying the composition of MMA and OMA/DMA in the initial feed. The details of feed compositions and polymer designations are given in Table 1. In subsequent discussions in the text these

Table 1 Copolymerisation of MMA with iso-octyl methacrylate (OMA) and iso-decyl methacrylate (MDA)

Monomer	Sample designation	Mole fraction of MMA in feed	% Conversion	Intrinsic viscosity dL/g	Mole fraction of MMA in copolymer
MMA	PMMA	1.0	6.2	0.57	1.0
OMA	POMA	0	8.7	0.748	0
	OM$_1$	0.25	6.5	0.25	0.184
	OM$_2$	0.75	8.9	0.53	0.662
	OM$_3$	0.87	11.9	0.62	0.813
DMA	PDMA	0	10.1	0.82	0
	DM$_1$	0.12	10.4	0.80	0.123
	DM$_2$	0.25	6.7	0.69	0.205
	DM$_3$	0.50	10.8	0.83	
	DM$_4$	0.75	9.7	0.75	0.717

designations have been used. In all cases polymerisation was carried to low conversion. The intrinsic viscosities of copolymers and homopolymers were determined in chloroform at 25° and these results are also given in Table 1. In general the intrinsic viscosity of copolymers was higher than PMMA but lower than POMA (in copolymers of MMA:OMA) or PDMA (in copolymers of MMA:DMA).

In Figs 1 and 2 the IR spectra of POMA and PDMA and copolymers are given. Characteristic peak due to ester group was observed at 1749 cm^{-1}. Other prominent absorption peaks were at 1450 and 1365 cm^{-1} ($C—CH_3$), 1220 and 1078 cm^{-1} (due to asym and sym C—O—C stretch). The peaks due to $—CH_2$ and $—CH_3$ stretch were observed at 2840–2998 cm^{-1}.

^{1}H-NMR spectra of PMMA, POMA and PDMA in $CDCl_3$ are given in Fig. 3. The peak at $\delta = 3.59$ ppm has been assigned to ester methoxy group. The signals that occur near $\delta = 1.0$ ppm are associated with protons of α-methyl group and those around $\delta = 1.82$ ppm are due to hydrogens of methylene groups. The location of these peaks depends on the configuration of the nearest neighbours. Thus the peak at 0.87 ppm arises from the methyl of a syndiotactic triad while the peak at 1.02 ppm is due to heterotactic triad. The occurrence of single methylene peak at 1.82 ppm is indicative of the racemic dyads. Since PMMA was prepared by free radical polymerisation, therefore the polymer is atactic and the quartet

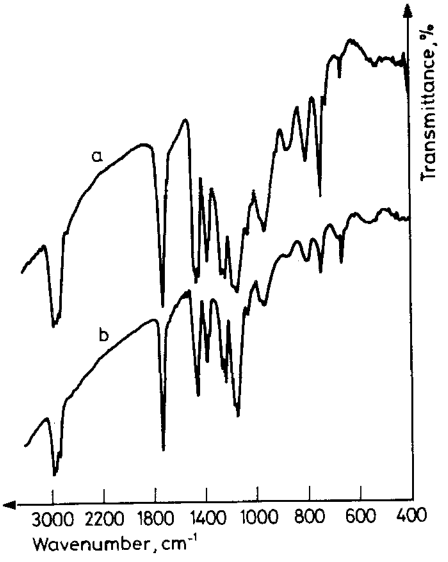


Fig. 1 FTir spectra of (a) poly iso-octyl methacrylate, (b) poly iso-decyl methacrylate

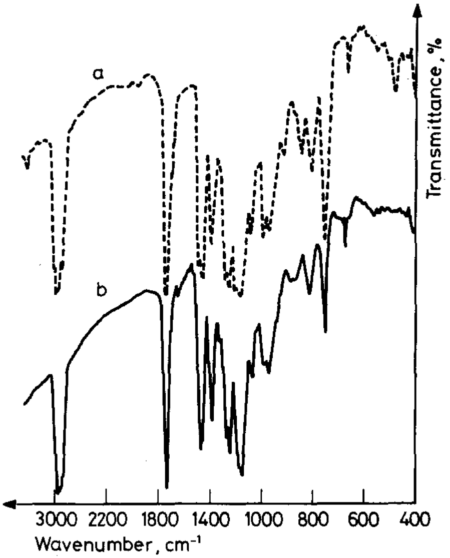
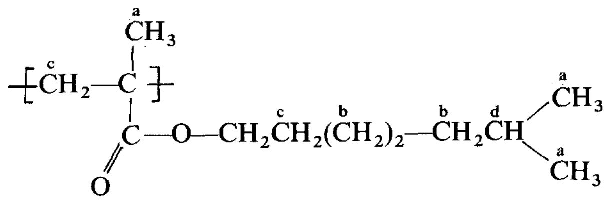


Fig. 2. FTir spectra of copolymers of MMA and DMA (a) sample DM_4, (b) sample DM_1

expected for an isotactic placement of methylene groups centered around 1.82 ppm was not observed.

In the ^1H–NMR spectrum of POMA peaks due to protons of alkyl side chain were also observed at $\delta = 0.877, 1.257, 1.57$ and 1.93 ppm, and arise due to methyl ("a" protons), —CH_2— (6H, "b" protons), "c" protons (4H) and "d" protons (1H), respectively.



The location of various signals in PDMA were at $\delta = 1.98, 1.59, 1.291$ and 0.879 ppm, and these can be explained as has been done for POMA.

The two hydrogens of —OCH_2— group present in iso-decyl and iso-octyl methacrylate produce a single peak around 3.93 ppm (Figs 3b and 3c), whereas the —OCH_3 group in PMMA gives a peak at 3.59 ppm. The area under these two peaks, was used to calculate the relative proportions (mole fractions) of the monomers in a given copolymer. The ^1H–NMR spectra of various copolymers are given in Figs 4–6. It is obvious from these figures that as the mole fraction of iso-decyl or iso-octyl methacrylate increased in the initial monomer feed, an increase in

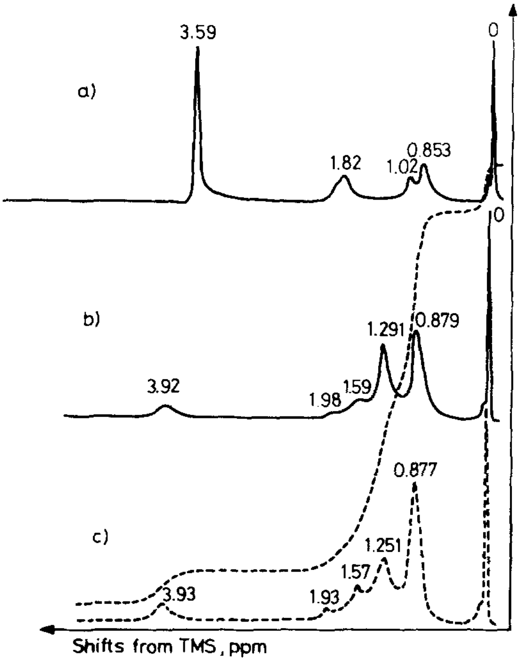


Fig. 3 ^{1}H-NMR spectra of (a) PMMA, (b) POMA, (c) PDMA

the area of peak at 3.93 ppm takes place. In Table 1, the composition of the copolymers thus obtained are given. The plot of mole fraction of MMA in the feed vs. mole fraction in the copolymer was found to be a straight line indicating thereby the random nature of these copolymerisations (Fig. 7).

Attempt was also made to characterise copolymer microstructure from the ^{1}H-NMR spectra. In these copolymers, one can divide the triads of repeat units in two groups of three, depending on the identity of central unit. Thus the centre of a triad can be bracketed by two monomers identical to itself $(M_1M_1M_1)$ different from itself $(M_2M_1M_2)$ or by one of each $(M_1M_1M_2)$. In each of these, therefore, the central repeat unit will be in a different environment and a characteristic proton in that repeat unit will resonate at a different location, depending on the effect of that environment. Thus if one considers the methoxy peak of PMMA as the central unit, then the position of this signal is expected to shift by the presence of iso-octyl methacrylate/iso-decyl methacrylate. A shift to lower field was observed in the location of methoxy peak by an increase in the OMA/DMA mole fraction in the copolymers. Similarly a shift in—OCH_2—signal of OMA/DMA was observed in copolymers. Figure 8 shows a plot of chemical shift (ppm) of methoxy proton vs. the mole fraction of MMA in the copolymers. A linear relationship is observed,

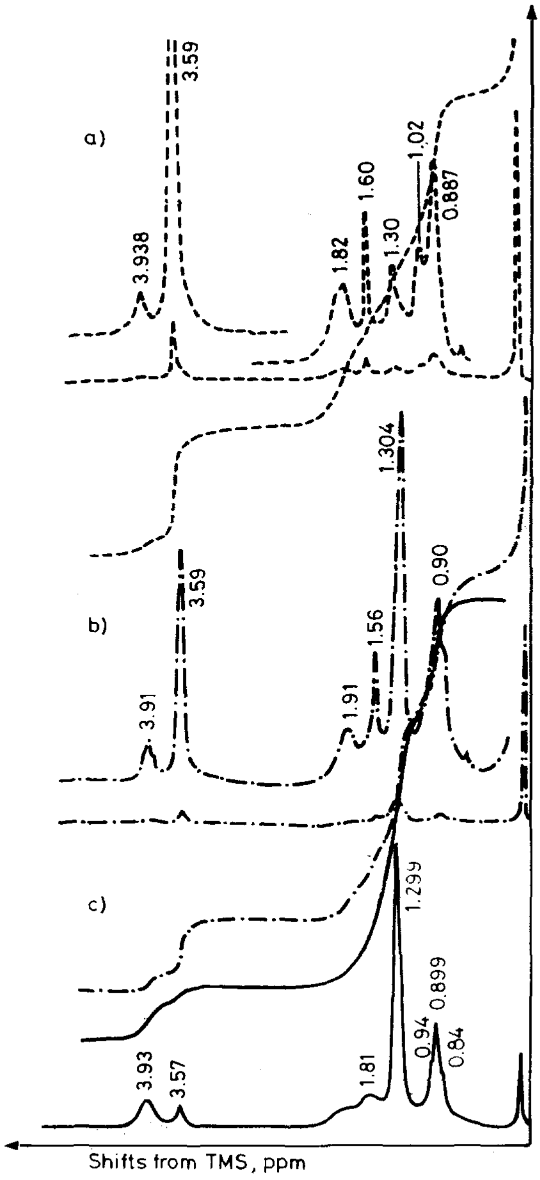


Fig. 4 ^{1}H-NMR spectra of copolymers of MMA and OMA (a) sample OM_3, (b) sample OM_2, (c) sample OM_1

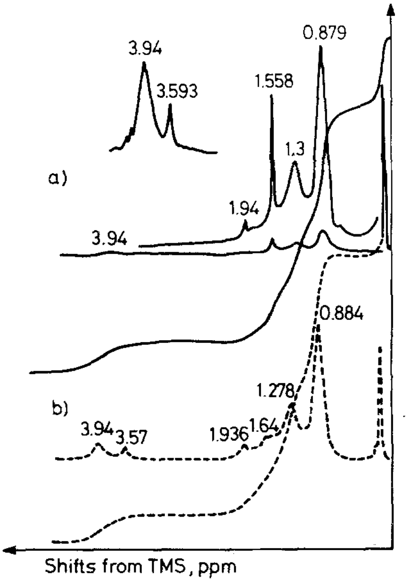


Fig. 5 ^{1}H-NMR spectra of copolymers of MMA and DMA (a) sample DM_1, (b) sample DM_2

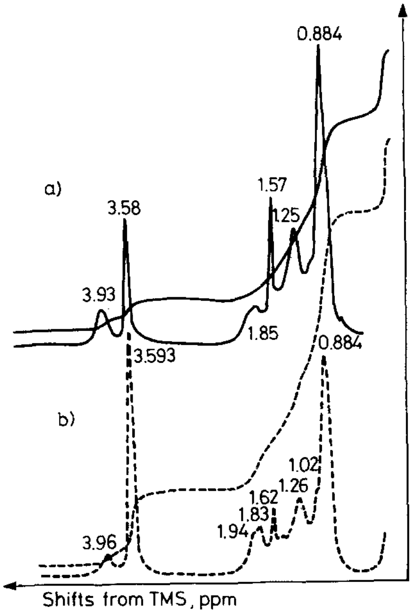


Fig. 6 ^{1}H-NMR spectra of copolymers of MMA and DMA (a) sample DM_3, (b) sample DM_4

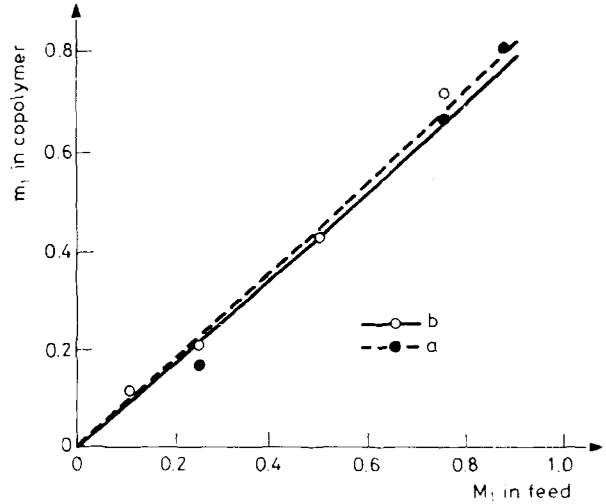


Fig. 7 Plot of mole fraction of MMA in the feed (M_1) vs. mole fraction of MMA in the copolymer (m_1)

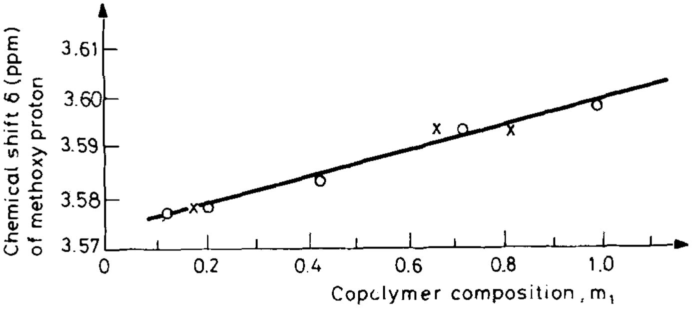


Fig. 8 Plot of chemical shift (δ) of methoxy protons vs. the mole fraction of MMA in the copolymers

implying thereby that from the location of methoxy peak one can also determine the copolymer composition.

The location of the various proton resonance signals observed in the copolymers and homopolymers of MMA and OMA/DMA are summarised in Table 2. In these ^{1}H-NMR spectra, peaks due to both comonomers were observed but there was a slight shift in the position of the signals.

Table 2 Position of various proton resonance signals in various polymer samples

Sample	Chemical shifts, δ, ppm							
PMMA	0.853	1.02	—	—	1.82	—	3.59	—
PDMA•	0.877	—	1.257	1.57	—	1.93	—	3.93
DM_1	0.879	—	1.3	1.558	—	1.941	3.576	3.946
DM_2	0.884	—	1.272	1.64	—	1.936	3.578	3.946
DM_3	0.879	1.149	1.257	1.571	1.85	—	3.583	3.931
DM_4	0.844	1.02	1.26	1.62	1.83	1.94	3.593	—
POMA	0.879	—	1.291	1.590	—	1.938	—	3.92
OM_1	0.899	0.94	1.299	1.610	1.81	—	3.57	3.93
OM_2	0.853	1.02	1.304	1.56	1.91	1.958	3.593	3.94
OM_3	0.862	1.02	1.3	1.60	1.828	—	3.595	3.938

Determination of monomer reactivity ratios

The change in the composition of the copolymer in the copolymerisation of MMA with the OMA/DMA can be expressed by the following equation:

$$\frac{m_1}{m_2}=\frac{r_1M_1^2+M_1M_2}{r_2M_2^2+M_1M_2} \tag{1}$$

where M_1 and M_2 are the concentration of monomers, $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ are the monomer reactivity ratios. The copolymer composition equation may be written as [9]:

$$r_2 = r_1\mathrm{H}^2/h+\mathrm{H}(1-h)/h \tag{2}$$

where, $\mathrm{H} = M_1/M_2$ and $h = m_1/m_2$.

Monomer reactivity ratios r_1 and r_2 can thus be calculated graphically by plotting H^2/h *vs.* $\mathrm{H}(1-h)/h$ (Fig. 9). The results of these calculations are given in Table 3. Reactivity ratio r_2 was found to be slightly higher than r_1 and these values indicate the random nature of these copolymerisations.

For further confirmation of the reactivity ratios Kelen–Tudos [10] and Joshi–Joshi [11] methods were also used to evaluate r_1 and r_2. According to Kelen–Tudos method, the Eq. (1) can be written as:

$$G/\alpha+F=(r_1+r_2/\alpha)F/\alpha+F-r_2/\alpha \tag{3}$$

where, $G = \mathrm{H}(h-1)/h$.

$$F=\mathrm{H}/h$$

$$\alpha=\sqrt{F_mF_M}$$

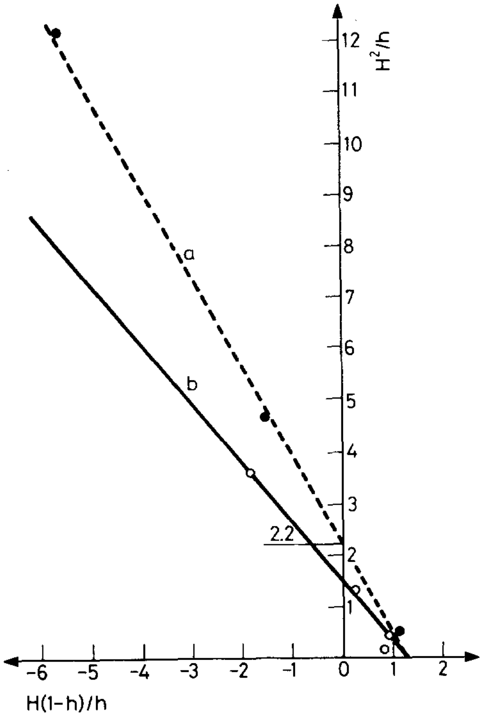


Fig. 9 Plots for determination of reactivity ratios by graphical method, for copolymers of (a) MMA and OMA, (b) MMA and DMA

Table 3 Monomer reactivity ratios of methyl methacrylate (M_1) and iso-octyl methacrylate/iso-decyl methacrylate (M_2)

Method	Comonomer	r_1	r_2
Graphical (based on Eq. (2))	OMA	0.58	1.28
	DMA	0.87	1.30
Kelen–Tudos	OMA	0.64	1.524
	DMA	0.66	1.08
Joshi–Joshi	OMA	0.48	1.34
	DMA	0.72	1.10

F_m stands for lowest and F_M for highest value. Plotting $G/\alpha+F$ as a function of $F/\alpha+F$, a straight line was obtained for the two sets of copolymers (Fig. 10), which when extrapolated to $F/\alpha+F = 0$ and $F/\alpha+F = 1$ gave $-r_2/\alpha$ and r_1 (both as intercepts).

The Joshi–Joshi equation, based on integrated copolymerisation equation, was also used to evaluate r_1 and r_2. In Table 3, r_1 and r_2 calculated by the different

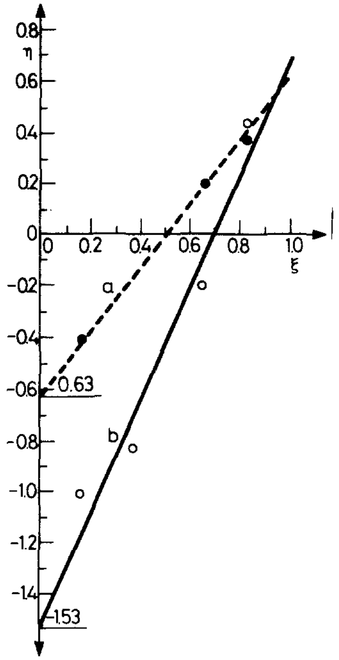


Fig. 10 Plots for determination of monomer reactivity ratios using Kelen–Tudos method, (a) MMA and OMA, (b) MMA and DMA

methods are given. There is a good agreement between the value calculated by these different methods; r_1 and r_2 values thus indicate that copolymerisation of methyl methacrylate with long chain alkyl methacrylates using the free radical polymerisation, produces a random copolymer.

The proton decoupled ^{13}C–NMR spectra of PMMA, POMA and PDMA were also recorded (Fig. 11). In PMMA splittings attributed to a sensitivity to configurational sequences are observed for all but methoxy carbon which appears as a singlet around 51.82 ppm. The methyl carbon appears around 18–21 ppm, the quarternary carbon around 44.5 ppm. The triad placements for both methyl and quarternary cabon atoms have been assigned as mm, mr and rr from low to high field [12]. The methylene carbon of the backbone gives a signal at 53–54 ppm in ^{13}C–NMR while the signal due to ester carbonyl appears at 175–178 ppm.

In PDMA the signal due to methoxy carbon at 51.82 ppm was not present instead a broad doublet (63.62 and 65.09 ppm) centered around 64.4 ppm was observed. In addition to ^{13}C resonance, signals due to carbon of long alkyl side chain were also observed in the region 10–40 ppm. The assignment for these carbons was done by using the additive shift parameters for hydrocarbons. In such calculations assumption has been made that the ester group does not influence the chemical shifts of the methylene groups.

The calculations were done using the formula $\delta = -2.5 + nA$ where δ is the predicted shift parameters and n is the number of carbon atoms for each shift parameter [13]. For PDMA δ could thus be predicted for all the ten carbons in the side chain beginning with the terminal methyls (δ_1) in the following manner δ_1 (two methyl groups) = 22.2, $\delta_2 = 28.4$, $\delta_3 = 39.3$, $\delta_4 = 27.4$, $\delta_5 = 31.0$, $\delta_6 = 30$, $\delta_7 = 29.4$, $\delta_8 = 29$, $\delta_9 = 64.9$ ppm. As mentioned earlier the O—CH signal was observed as a doublet centered around 64.4 ppm. Similar calculations were also done for POMA and chemical shift was found to be $\delta_1 = 22.2$, $\delta_2 = 26.4$,

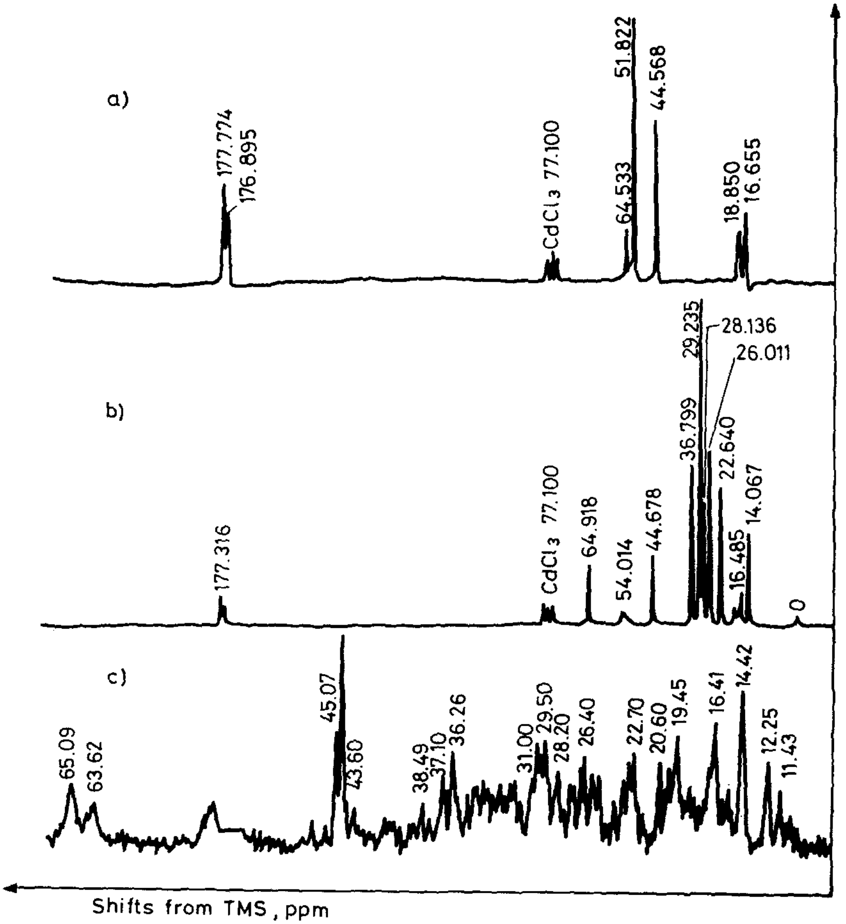


Fig. 11 Proton decoupled ^{13}C-NMR spectra of (a) PMMA, (b) POMA, (c) PDMA

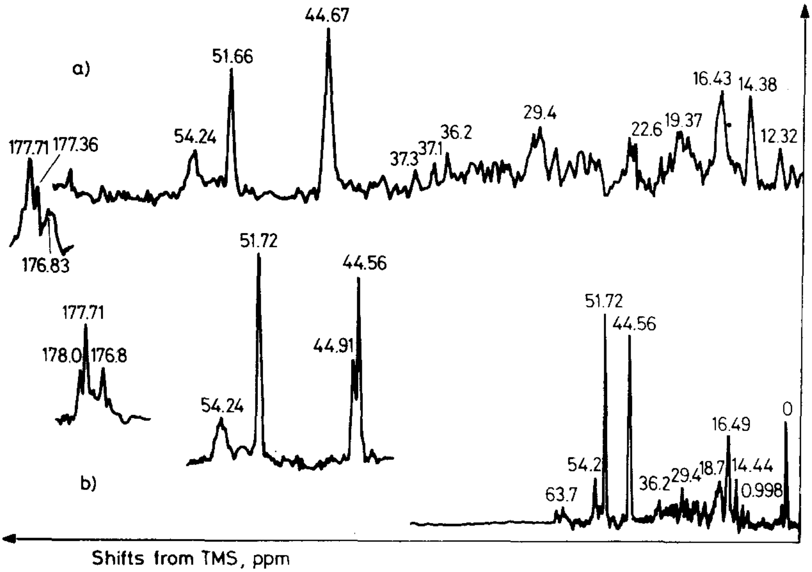


Fig. 12 Proton decoupled ^{13}C–NMR spectra of copolymers of MMA and DMA (a) sample DM$_3$, (b) sample DM$_4$

$\delta_3 = 39.2$, $\delta_4 = 27$, $\delta_5 = 29.6$, $\delta_6 = 29.1$ and $\delta_7 = 64.9$ ppm. The calculated and the observed values for other peaks were also in agreement (Fig. 11).

In the copolymers (Fig. 12) the characteristic features for PMMA (signal at 51.77 ppm) and for OMA/DMA (around 63 and 65 ppm) were observed. However, since the spectra were very complicated due to the presence of long alkyl chains, sequence determination was found to be very complicated and, therefore, has not been done.

Thermal behaviour

Thermogravimetric analysis of the polymer samples showed that these were stable upto 250° and started losing weight in the temperature range of 250–400°. PMMA showed a two step decomposition with T_{max} values at 290.5° and 358.6° (Table 4). This sort of behaviour has been observed by previous workers and has been attributed to the initiation of depolymerization from the weak sites in PMMA at a lower temperature. At higher temperature, random scission is believed to take place. In POMA and PDMA a single step degradation with T_{max} less than that of PMMA was observed (Figs 13 and 14). FDT was also found to be lower 323° and 315°, respectively. This could probably be due to the possibility of degradation of the side chain, along with degradation of the main chain. In the copolymers of

Table 4 Results of thermogravimetric analysis of polymer samples

Sample	IDT, °C	T_{max-1}, °C	T_{max-2}, °C	T_{max-3}, °C	FDT, °C
POMA	270.8		300.1	—	323.0
OM_1	279.7		315.7	—	330.2
OM_2	252.1		270.5	—	312.2
OM_3	217.5	254.8	300.0	370.9	393.1
PMMA	252.0	290.5	358.6	—	379.4
PDMA	263.0		301.4	—	315.0
DM_1	254.2		295.3	—	316.7
DM_2	263.8		302.5	—	323.3
DM_3	261.7		296.7	—	317.6
DM_4	211.6	250.2	344.2	—	390.6

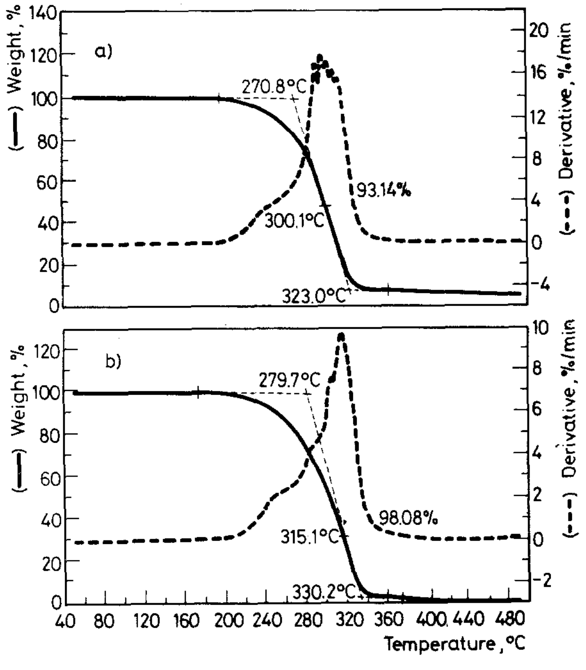


Fig. 13 Thermogravimetric traces of (a) poly iso-octyl methacrylate (POMA), (b) sample OM_1

MMA with OMA/DMA having highest MMA content (samples OM_3 and DM_4) a three step and two step decomposition was observed. As the concentration of MMA was lowered in the copolymers, a single step degradation (samples OM_2 and DM_3) was observed. An increase in OMA/DMA concentration (samples OM_3 to OM_1 and DM_4 to DM_1) brought about an increase in IDT and a decrease in T_{max} of the various copolymers.

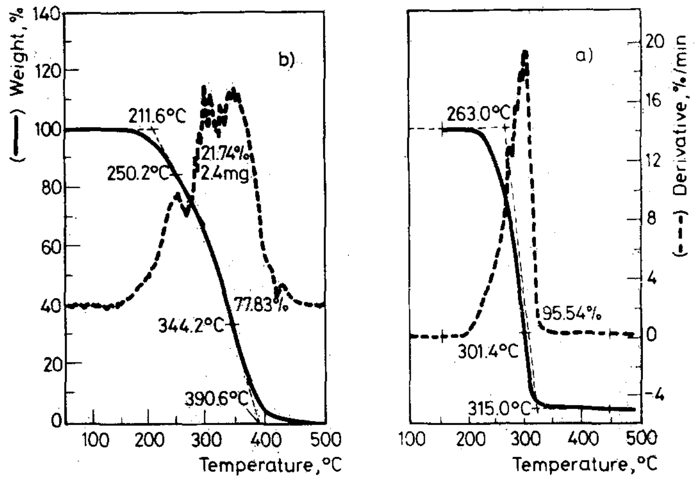
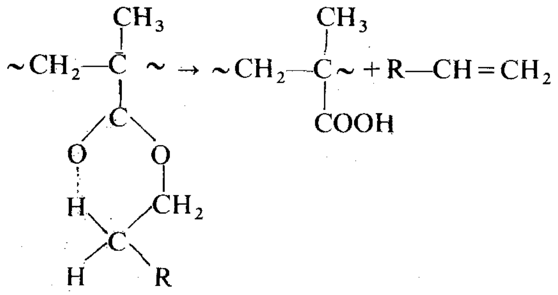


Fig. 14 Thermogravimetric traces of poly iso-decyl methacrylate (PDMA), (b) sample DM_4

Pyrolysis of PMMA leads to depolymerisation and quantitative monomers (MMA) is obtained. However, in alkyl methacrylate having long alkyl side chain, along with the monomer formation, side group elimination can also take place according to the following scheme:



Therefore, along with monomer, alkenes (iso-octene-I or iso-decene I) are also expected to be formed. In order to understand this behaviour, electron induced fragmentation pattern of polymers pyrolysed at the ion probe were analysed.

The mass spectrum of volatile products obtained on pyrolysis of PDMA is given in Fig. 15a. The molecular ion peak was observed at $m/e = 228$, whereas the molecular weight of decyl methacrylate is 226. The presence of molecular ion peak at $M+2$ position is indicative of a hydrogen addition to the olefinic bond either during fragmentation or at a later stage. Appearance of m/e 228, indicates formation of monomer during the pyrolysis. If side chain elimination had occurred iso-decene would have been formed ($m/e = 140$). However, no fragment ion was observed at

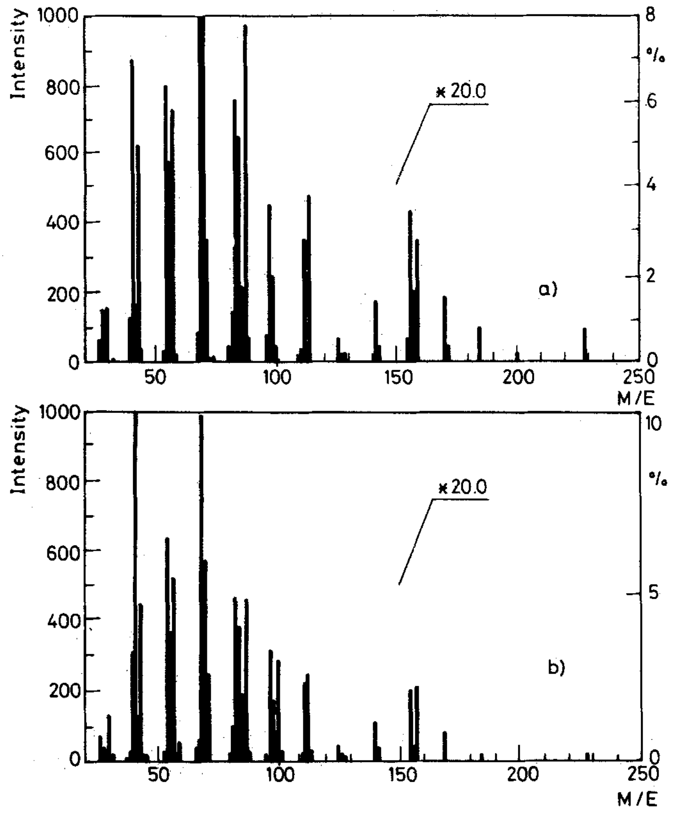
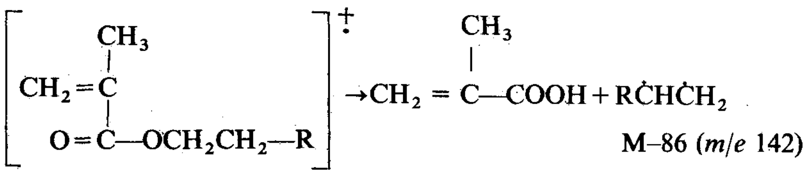


Fig. 15 Mass spectra of (a) poly iso-decyl methacrylate (PDMA), (b) sample DM_4

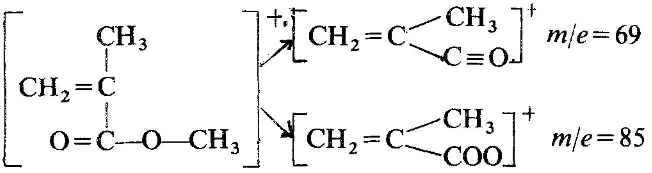
m/e 140. The fragment ion observed at m/e 142 can be explained by McLafferty rearrangement in the following manner:



$$\left[\begin{array}{l}\quad\ \mathrm{CH_3}\\ \quad\ \ |\\ \mathrm{CH_2{=}C}\\ \quad\ \ |\\ \quad\mathrm{O{=}C{-}OCH_2CH_2{-}R}\end{array}\right]^{+\cdot} \rightarrow \mathrm{CH_2} = \overset{\displaystyle \mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{{-}COOH} + \mathrm{R\dot{C}H\dot{C}H_2}$$

M–86 (m/e 142)

The parent ion peak in the pyrolysis of PMMA appeared at m/e 100 and is, therefore assigned to formation of MMA. Base peak was observed at m/e 69. This peak is a characteristic peak for esters and arises due to following fragmentation pattern.



Mass spectra of copolymers of MMA with DMA/OMA (Figs 15b, 16a and 16b) showed the molecular ion peaks of both MMA ($m/e = 100$) and DMA/OMA ($m/e = 228$ and $m/e = 198$). The fragmentation pattern was a combination of that due to both these monomers. In addition to this it was found that for DM_4 (Fig. 15b) the relative abundance of fragment ion at m/e 100 was much higher than that of m/e 228. As the concentration of DMA was increased, (Fig. 16a), the relative abundance of fragment ion at m/e 228 increased and that at m/e 100 decreased,

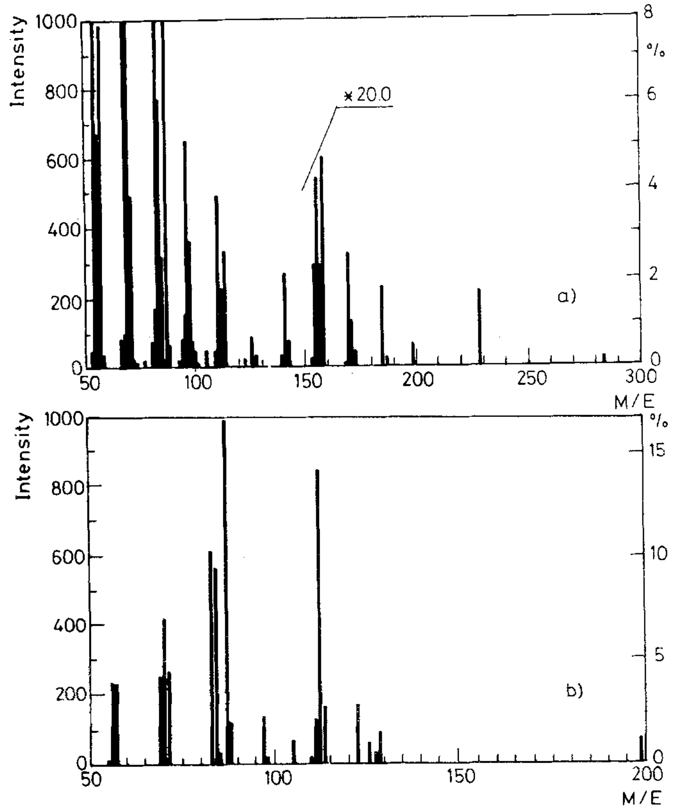


Fig. 16 Mass spectra of (a) sample DM_2, (b) sample OM_1

thereby indicating that copolymer composition determines the relative abundance of the fragment ions.

In order to further ascertain the degradation mechanism, PY–GC of PMMA, POMA, PDMA was carried out. In this the fractions obtained after pyrolysis of polymers are separated due to the difference in their boiling points, as a nonpolar column heated at a programmed rate is used. A single peak was observed in the chromatograms of PMMA, PDMA and POMA, thereby indicating that no further fragmentation occurs after pyrolysis. Retention times for PMMA, POMA and PDMA were found to be 1.05 min, 16.04 min and 20.43–21.83 min respectively.

On the basis of above studies it can, therefore, be concluded that copolymers of MMA with OMA and DMA prepared by free radical polymerisation are random in nature. The composition of such copolymers can be determined by ^{1}H–NMR spectroscopy. Thermal degradation of alkyl methacrylate based on C_8 or C_{10} alcohol proceeds predominantly by loss of monomer (depolymerization).

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Zusammenfassung — Mittels dynamischer Thermogravimetrie, Massenspektroskopie und Pyrolysengaschromatographie wurde das thermische Verhalten von Kopolymeren aus Methylmethacrylat (MMA) und Isooktyl/Isodecyl-methacrylat untersucht. Die Kopolymerproben waren bis 250 °C stabil. Ein vollständiger Gewichtsverlust wurde bei 400 °C beobachtet. Der Abbau sowohl der Homopolymere als auch der Kopolymere erfolgt durch eine überwiegende Abgabe von Monomeren.

Резюме — С помощью динамической термогравиметрии, масс-спектроскопии и пиролизной газовой хроматографии изучено термическое поведение сополимеров метилметакрилата и изооктил/изо-децилметакрилата. Сополимеры устойчивы до температуры 250°. Полная потеря веса происходит при температуре около 400°. Деградация гомополимеров, также как и сополимеров протекает с преобладающей потерей мономера.