

THERMAL BEHAVIOUR OF COPOLYMERS OF METHYL METHACRYLATE AND 2-ETHYLHEXYL METHACRYLATE

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Five copolymer samples containing different mole fractions of methyl methacrylate (MMA) and 2-ethylhexyl methacrylate (EHMA) were prepared by bulk polymerisation at 70°C using 0.2% benzoyl peroxide as an initiator. The copolymer composition was determined by ¹H NMR spectroscopy. Molecular weight of copolymers was determined by gel permeation chromatography and viscosity measurements. Thermogravimetric experiments were conducted to evaluate activation energy for the degradation of copolymers. Two to four reaction stages for the weight loss were observed in the copolymers. A decrease in thermal stability was observed by an increase in EHMA content.

Poly(methyl methacrylate) (PMMA) is a versatile, hard, rigid, transparent plastic material having extremely good weathering resistance. In order to extend the potential application areas of PMMA in building and construction and outdoor applications, considerable work has been done to improve fire resistance, impact behaviour and heat distortion temperature. Copolymerisation of methyl methacrylate (MMA) with suitable vinyl monomers such as alkyl methacrylates has been carried out for modifying the properties of the polymer [1-4]. The length of alkyl group in these alkyl methacrylate has a pronounced effect on the flexibility of methacrylate polymers. Whereas the usual effect of increasing the side chain length in the esters derived from straight chain alcohol is to soften the polymer and to make it more flexible, the branched chain alcohols have the opposite effects [5]. The presence of comonomers in PMMA backbone may also affect its thermal behaviour.

Although significant amount of work has been carried out on thermal and oxidative degradation of PMMA [6-12], only little attention has been

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focussed on thermal behaviour of methacrylate copolymers. The objective of the present work was to study the effect of structure on thermal degradation of copolymers of MMA and 2-ethylhexyl methacrylate (EHMA). Five copolymer samples were prepared by varying the ratio of MMA and EHMA in the initial monomer feed. Thermal behaviour of the copolymers was investigated by dynamic thermogravimetry.

Experimental

EHMA (Fluka AG) and MMA (Fluka AG) was purified by washing with 5% NaOH followed by water. The monomers were dried overnight over anhydrous Na₂SO₄ and distilled under reduced pressure. Benzoyl peroxide (BPO) (Loba-Chemie), recrystallized from chloroform-methanol system was used as an initiator.

Copolymerisation of MMA with EHMA was carried out in bulk at 70° using 0.2% (W/V) BPO as an initiator. Five different monomer ratios were taken in the initial feed, and the reaction was carried out for 40-60 min so as to keep conversion below 10%.

Structure characterization of copolymers was done by recording the ¹H NMR spectra in CDCl₃ at room temperature using Jeol JNM-FX 100 FT NMR spectrometer and tetramethyl silane as an internal standard.

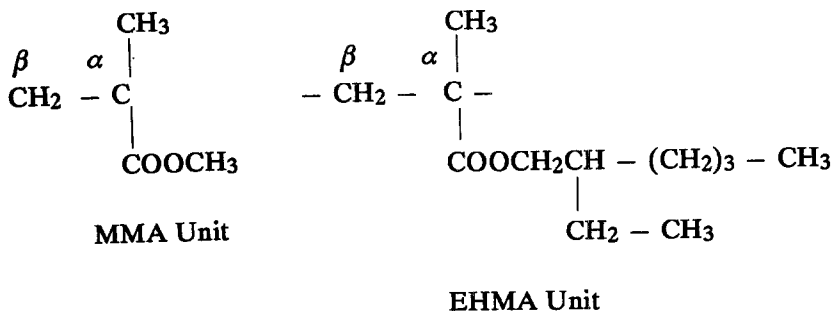
Intrinsic viscosity [η] of the samples was determined in chloroform at 30° using Ubbelohde suspension level viscometer.

Molecular weight and molecular weight distribution of the copolymers was determined by Gel Permeation Chromatography using a Waters Associates GPC having a PL gel 5 μ mixed GPC column. PMMA reference standards were used for calibration.

Thermal behaviour of the samples in nitrogen atmosphere (flow rate 60 cm³/min) was evaluated using DuPont 1090 thermal analyzer having 951 TG module. A heating rate of 4, 7, 10, and 15 deg/min and a sample size of 12 \pm 1 mg was used.

Results and discussion

The copolymer composition was determined by ¹H NMR spectroscopic technique. The main chain of MMA and EHMA is represented as follows:



Since both the monomers are alkyl ester of methacrylic acid, the characteristic chemical environment of α -methyl and β -CH₂ protons is identical even though the alkyl group differs in MMA and EHMA. The identifiable difference corresponds to -OCH₂ group in EHMA which produces a signal at δ 3.84 ppm while the -OCH₃ group of MMA is observed as singlet at δ 3.59 ppm.

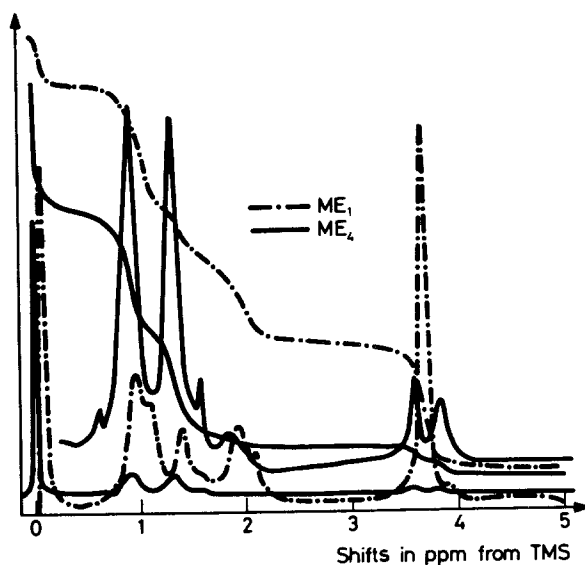


Fig. 1 ¹H NMR spectra of ME₁ and ME₄ copolymers in CDCl₃

The other methyl and methylene protons of alkyl side chain in EHMA appear at high field. It is obvious from Fig. 1 that as the mole fraction of EHMA is increased in initial feed an increase in area of peak at 3.84 ppm is observed. Therefore, the molar ratio of monomer in copolymers can be calculated from the ratios of the peak area at 3.59 ppm (corresponding to 3H of $-OCH_3$ group of PMMA) and δ 3.84 ppm (due to 2H of $-OCH_2$ group of EHMA). This method for determining copolymer composition has been reported earlier [3-4]. The particular advantage of this method of determining copolymer composition is that it is a simple and rapid technique. In Table 1 the composition of monomer feed and copolymer and designation of copolymer samples is given.

Table 1 Copolymerisation of MMA with EHMA

Sample designation	Mole fraction of MMA in feed	Mole fraction of MMA in copolymer	% age conversion
ME ₁	0.9010	0.8916 (0.8155)	7.9
ME ₂	0.7010	0.7097 (0.5548)	10.2
ME ₃	0.5021	0.5532 (0.2766)	8.5
ME ₄	0.2998	0.3478 (0.0760)	11.2
ME ₅	0.1029	0.1429 (0.0227)	15.0

(Figures in parenthesis indicate copolymer composition determined from 1H using Grassie's method)

A plot of mole fraction of MMA in feed vs. mole fraction of MMA in copolymer is given in Fig. 2. An increase in M_1 results in an increase in m_1 in copolymer thereby indicating that the monomer EHMA:MMA undergoes ideal copolymerization giving random copolymer.

However, the disadvantage of this method for determination of copolymer composition is that it is sometimes very difficult to accurately determine the area of $-OCH_3$ and $-OCH_2$ peaks both of which appear distinctly at low field. This problem is aggravated when the molar composition of one of the components is low (Fig. 1). In such cases it is very difficult to determine the area accurately and thus an element of error may be introduced in determination of copolymer composition.

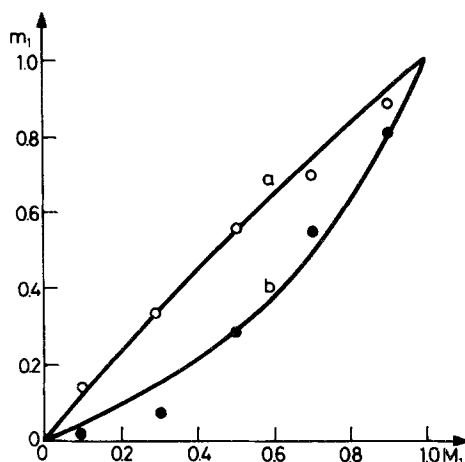


Fig. 2 Plot of mole fraction of MMA (m_1) in the copolymers vs. mole fraction of MMA (M_1) in the feed. Copolymer composition calculated (a) from the peak area ratio at δ 3.84 and 3.59 ppm (b) using Grassie method

In order to overcome this difficulty, the method of Grassie *et al.* reported earlier was used to determine copolymer composition. In this approach, used for determining composition of MMA-MA copolymer [13] and ethyl acrylate, *n*-butyl methacrylate copolymers [14] the ratio of intensities of down field protons to that of the total protons is determined. Using this technique the composition of MMA:EHMA copolymers was also determined by adopting following procedure.

Let m_1 represent mole fraction of MMA in copolymer and $1-m_1$ that of EHMA. The total protons in each monomeric unit is in the ratio of 4:11 (MMA:EHMA). The ratio of downfield proton ($-\text{OCH}_3$ and $-\text{OCH}_2$) to that of total protons therefore, will be

$$3m_1/8 + (1-m_1)/11 = C$$

$$\text{or } m_1 = (88C-8)/25$$

The ratio of downfield protons to that of total protons was calculated from the ^1H NMR spectra of all copolymers and thus copolymer composition was calculated. The values thus determined are also reported in Table 1 in parenthesis. The copolymer composition determined by this method shows a lower mole fraction of MMA in copolymer compared to the method based on peak area of $-\text{OCH}_3$ and $-\text{OCH}_2$ protons. This discrepancy in the

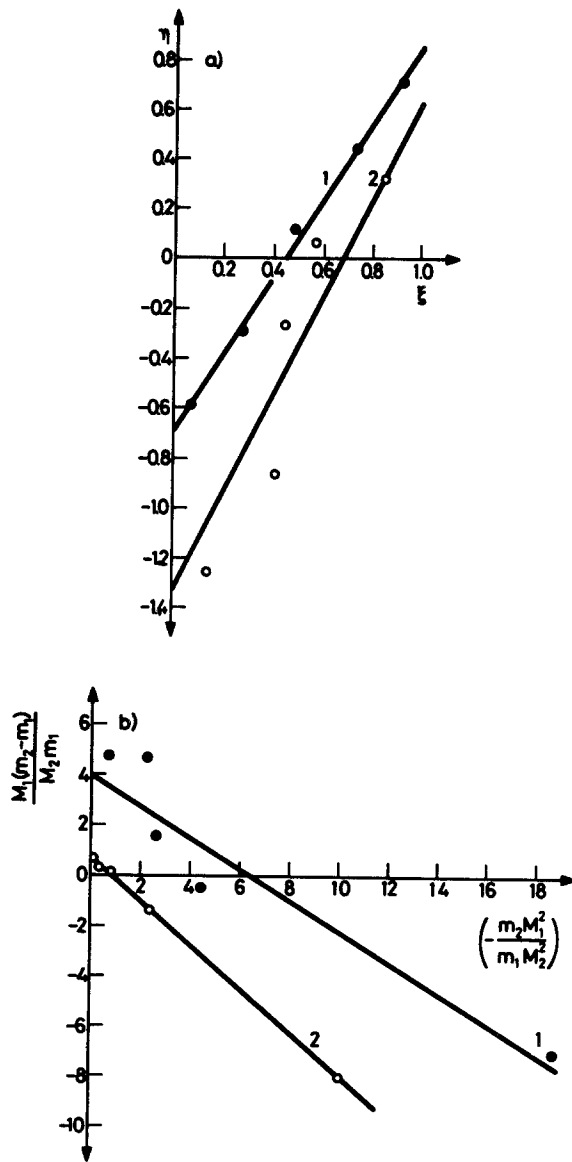


Fig. 3 (a) Kelen-Tüdös plot (b) Fineman-Ross method for determination of reactivity ratios. Copolymer composition determined (1) using Grassie's method, (2) from the ratio of peak area at δ 3.84 and 3.59 ppm

data is difficult to explain and may be attributed to the errors involved in integration. A plot of m_1 , vs. M_1 using this data has also been plotted (Fig. 2) and a random copolymerization is indicated.

The copolymer composition determined using Grassie's method as well as $\text{OCH}_2:\text{OCH}_3$ proton ratios were used for calculating reactivity ratios by using Finemann-Ross [15] and Kelen-Tüdös method [16] (Fig. 3). The values are tabulated in Table 2. The r_1 values are comparable but a significant difference is obtained in r_2 .

Table 2 Monomer reactivity ratios of MMA (m_2) and EHMA (m_2)

Method	Copolymer composition determination	r_1 (MMA)	r_2 (EHMA)
Graphical	Grassie's method	0.627	4.334
Kelen-Tüdös		0.61	4.333
Graphical	$\text{OCH}_2:\text{OCH}_3$ proton ratio	0.864	0.698
Kelen-Tüdös	method	0.860	0.636

The molecular weight of the copolymers was determined by the gel permeation chromatography. A typical chromatogram for sample ME_1 is shown in Fig. 4. The molecular weights of various copolymers and homopolymers are given in Table 3. All the polymers had high molecular weight and molecular weight distribution ranged from 1.24 to 1.32. Intrinsic viscosity of copolymers and homopolymers in CHCl_3 was also determined and results are given in Table 3.

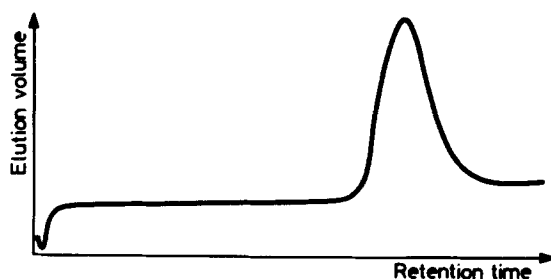
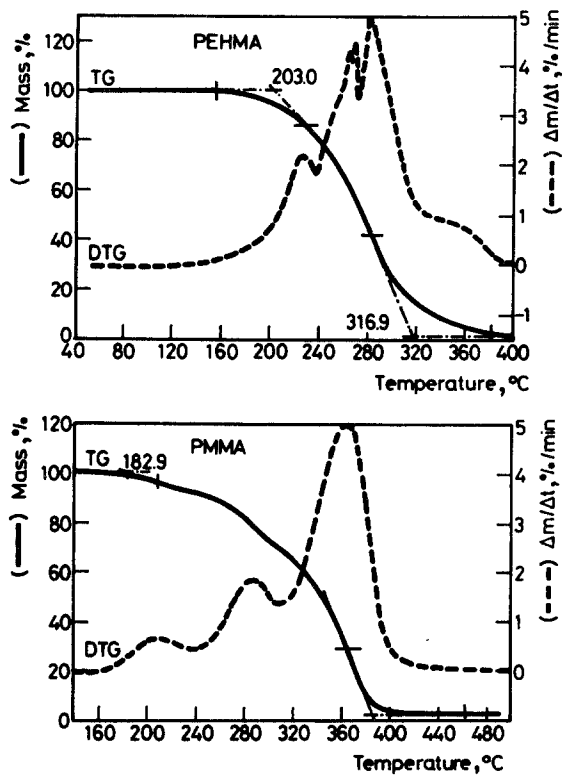


Fig. 4 Gel permeation chromatogram of ME_1

Table 3 Molecular weight and intrinsic viscosity (in CHCl_3) of various copolymers of MMA and EHMA

Sample designation	\bar{M}_w	\bar{M}_n	MWD	$[\eta]$ dl/g
ME ₁	341000	255000	1.34	1.69
ME ₂	365000	287000	1.27	1.32
ME ₃	487000	392000	1.24	1.46
ME ₄	466000	356000	1.31	1.46
ME ₅	525000	398000	1.32	1.90

**Fig. 5** TG traces of PMMA and PEHMA in nitrogen atmosphere at a heating rate of 4 deg/min

Thermal behaviour

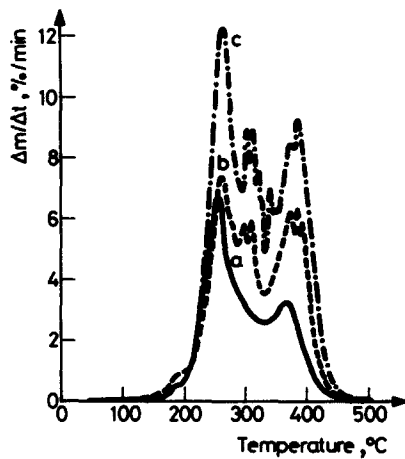


Fig. 6 DTG traces of ME₁ in nitrogen atmosphere at a heating rate of (a) 7 (b) 10 and (c) 15 deg/min

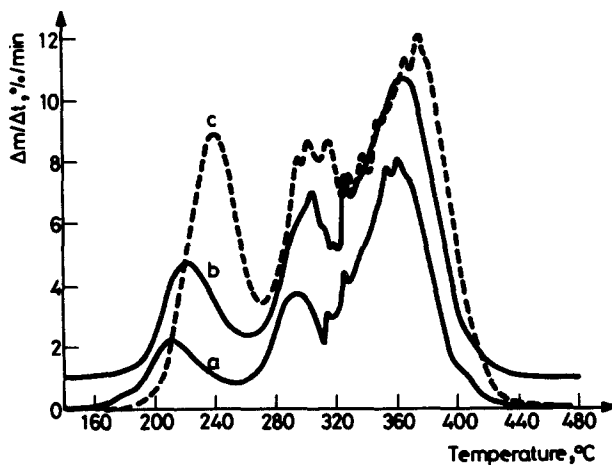


Fig. 7 DTG traces of ME₂ in nitrogen atmosphere at a heating rate of (a) 7 (b) 10 and (c) 15 deg/min

Typical results for TG and derivative thermogravimetry (DTG) for homopolymers in nitrogen atmosphere are shown in Fig. 5. The DTG curve for PMMA shows 3-4 stages of degradation. The first reaction is observed as a small peak around 210°. The main reaction stage is observed above 300°. Similar multiplicity of peaks in DTG trace has earlier been reported for PMMA [6-8] McNeil has attributed the main reaction of PMMA degradation (third stage) due to unzipping initiated by random scission. The first reaction stage is initiated by scissions of head-to-head linkages, the second step by scissions at the chain-end initiation [17]. Similar multistage degradation was observed in copolymers.

TG measurements of PMMA, poly (2-ethylhexyl methacrylate) (PEHMA) and copolymers ME₁, ME₂ and ME₃ were done at four different heating rates to determine activation energy (*E*) for the various steps of degradation. Differential method based on rate of weight loss was used for determining *E*. The DTG traces of ME₁ and ME₂ degraded in nitrogen atmosphere are shown in Figs 6 and 7. An increase in rate of heating resulted in an increase in temperature of peak maxima and also the peak height. Kissinger method [17] was used to determine kinetic constants.

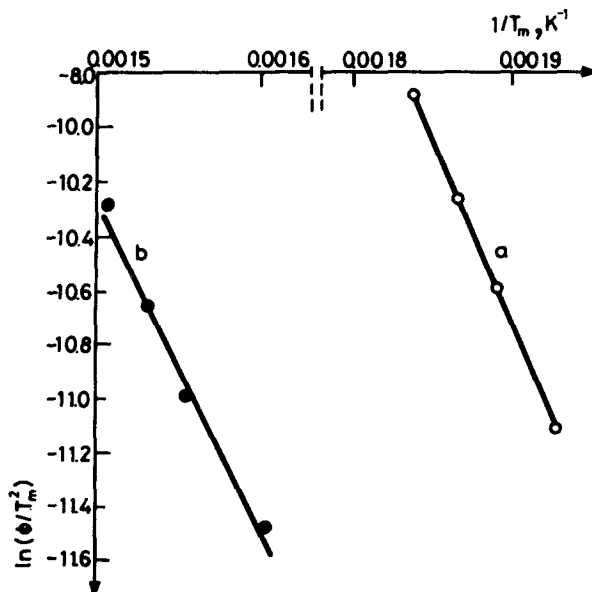


Fig. 8 Kissinger plot of ME₁ degraded in nitrogen atmosphere in the temperature range (a) 200°-300°C (b) 325-450°C

$$\ln(\Phi/T_m^2) = \ln(nRAW_m^{n-1}/E) - (E/RT_m)$$

where Φ is the heating rate, T_m is the temperature at the maximum rate of weight loss, R is universal gas constant, A is the preexponential factor, W_m is the weight of sample at the maximum rate of weight loss and n is the apparent order of reaction with respect to sample weight. The value of E was calculated for different steps by plotting $\ln(\Phi/T_m^2)$ vs. $(1/T_m)$ (Fig. 8). The activation energy values are given in Table 4. The activation energy for main stage decomposition (DTG peak at 360°) of PMMA has been reported as 210 kJ/mol [8] and for first and second step observed at 165 and 270° in DTG as 31 kJ/mol. The E values determined in present work for PMMA were found to be 39.70, 129.01 and 184.04 kJ/mol for first, second and third stages of degradation. These values thus agree well with the reported results. The activation energies for various steps for copolymer degradation are also given in Table 4. An increase in EHMA content in copolymers resulted in a decrease in temperature of decomposition but no systematic effect of copolymer composition on activation energy was observed.

Table 4 Activation energy for degradation of PMMA and its copolymers with EHMA in nitrogen atmosphere

Polymer sample	Temperature range, °C	Activation energy (E), kJ/mol
PMMA	140-260	39.70
	240-330	129.01
	290-430	184.94
ME ₁	200-300	114.6
	325-450	100.08
ME ₂	180-270	10.72
	260-330	115.17
	320-420	200.22
ME ₃	185-225	102.03
	225-260	97.34
	230-350	85.41

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Zusammenfassung – In einer Massepolymerisation bei 70° C wurden unter Anwendung von 0.2 % Benzoylperoxid als Initiator fünf Kopolymerproben mit jeweils unterschiedlichen Molenbrüchen von Methylmethacrylat (MMA) bzw. 2-Ethylhexylmethacrylat (EHMA) hergestellt. Die Zusammensetzung der Kopolymere wurde mittels ¹H-NMR Spektroskopie ermittelt. Das Molekulgewicht der Kopolymere wurde durch Gel-Permeations-Chromatographie und Viskositätsmessungen bestimmt. Zur Ermittlung der Aktivierungsenergie für die Degradation der Kopolymere wurden thermogravimetrische Untersuchungen angestellt. Für den Masseverlust der Kopolymere wurden je 2 bis 4 Reaktionsschritte beobachtet. Bei steigendem EHMA-Gehalt konnte ein Abnehmen der thermischen Stabilität festgestellt werden.