X-ray Diffraction Study of the Changes Induced During the Thermal Degradation of Poly (Methyl Methacrylate) and Poly (Methacryloyl Chloride)

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Poly (methyl methacrylate) – PMMA – and poly (methacryloyl chloride) – PMACl – were synthesized by free radical solution polymerization. The thermal stabilities of these polymers were determined with the help of thermogravimetry and differential thermal analysis. The structural changes in these materials at different temperatures (90, 140, 220 and 410 °C) were studied by X-ray diffraction. These studies indicate that PMACl is less amorphous than PMMA due to the presence of bulky chloride groups.

Introduction

The wide ranging applications of poly (methyl methacrylate) - PMMA – and allied polymers are well documented [1,2]. These polymers unlike ionic and metallic crystals and low molecular weight substances consist of long chain molecules arranged in aggregates, which assume complex shapes and structures. Many uses of polymers involve elevated temperatures, thus necessitating the determination of the structural changes that take place at these high temperatures [3]. The structural information gives an insight into the physical and mechanical properties of polymers [4]. The application of X-rays in material analyses makes it possible to determine detailed information on the state of order and disorder of the system [4-6]. Recently Saini [7] and Spevacek [8] utilized XRD for the characterization of PMMA.

In this paper, the structural changes occurring in PMMA and poly (methacryloyl chloride) - PMACl – when subjected to heat were studied employing X-ray diffraction.

Experimental

Synthesis of PMMA: PMMA was synthesized by solution polymerization in methanol of freshly purified monomer on a vacuum line (10^{-5}torr) using 0.05% w/v azo bis isobutyronitrile (AIBN) as a free radical initiator. The polymerization was carried out in water bath kept at 60 °C. The contents of the dilatometer were poured in constantly stirred diethyl ether to precipitate PMMA. After drying in a vacuum oven for 24 h, the sample was characterized [5,9] by infrared (IR) and nuclear magnetic resonance (NMR) spectroscopies.

The IR spectrum of PMMA showed strong peaks for C=O at 1720-1740 cm^{-1} and –C-O at 1020-1030 cm^{-1} and medium (sharp) for C-H at 2925-2945 cm^{-1}. A medium C=C peak at 1630 cm^{-1} was absent, indicating the formation of polymer. The NMR spectrum showed singlets at δ=1.5, δ=2.3 and δ=3.6 for ethylene, methyl and methoxy protons respectively [5].

Synthesis of PMACl: Freshly purified methacryloyl chloride and toluene was vacuum distilled into a dilatometer containing 0.05% w/v AIBN. The polymerization under vacuum (10^{-5} torr) at 60 °C was stopped after 4 h by pouring the reaction mixture in diethyl ether. The precipitated polymer was characterized by IR and NMR after drying in a vacuum oven for 24 h. The IR spectrum showed strong peaks at 1800, 1500, 1440 and 840 cm^{-1} resulting from C=O and C-Cl groups. Olefinic peaks at 1630 cm^{-1} were absent [10].

Thermal analysis: TG and DTA curves of samples were recorded on a DT 30B (Shimadzu, Japan) thermal analyzer. The polymers were heated at 10 °C/min from ambient temperature to 500 °C in a dynamic nitrogen atmosphere with a flow rate of 50 Ml/min.

X-ray diffraction studies: A Philips PW1450/70 X-ray diffractometer equipped with a PW1390 channel control goniometer and an argon – filled proportional counter was used for recording the diffractograms. Radiation was generated from a copper anode tube (Cu Kα 1.5418°A) using a Philips PW1730 X-ray generator operated at 40 kV and 30 mA.

Pyrolysis of polymers: Samples were heated at a heating rate of 10 °C/min in a tube furnace model RO7/50 supplied by Heraeus (Germany) up to temperatures of 90, 140, 220 and 410 °C. Each sample was kept at the required temperature for 15 min.

Results and Discussion

Before studying the thermal effects on these polymers, thermal stabilities and degradation patterns were determined by employing TG and DTA. It is evident from Figure 1 that PMMA decomposes in 2 stages, i.e. degradation of allylic chain ends followed by main chain scission [11]. The polymer starts to degrade at 200 °C, followed by a second stage commencing at 340 °C. The DTA curve also shows peaks in the same temperature regions. The DTA peak appearing at 130 °C, where no weight loss occurs, can be attributed to phase transitions. A similar peak is observed in DTA curves of PMACl reproduced in Figure 2 at 150 °C. The polymer is stable up to 270 °C beyond which it degrades via 2 stages. The endotherms with maxima at 292 °C and 425 °C represent the decomposition of PMACl.

In light of the results obtained by TG and DTA experiments, these samples were subjected to heating in a tube furnace at 90 °C, 140 °C, 220 °C and 410 °C. The samples were kept at limit temperatures for 15 min. XRD patterns were recorded at the end of each thermal cycle (heating stage) to assess the changes in these materials.

The XRD patterns of PMMA and PMACl samples are reproduced in Figures 3 and 4 respectively. These figures show diffuse halos at lower 2θ values, which is typical of amorphous polymers. The 'degree of amorphousness', i.e. disorder in polymer chains, is obtained by an arbitrary measure of the radial intensity distribution assuming that the more random and amorphous it is, the broader will be the halo. The radial width at one half maximum intensity might be used as a parameter for comparison. It must be kept in mind that it is only for comparison and is of no theoretical significance. It is evident from the data presented in Table that PMMA is more amorphous than PMACl. This may be explained based on the assumption

that the pendant groups in PMACl are better aligned around the polymer backbone than the methoxy groups (having greater stearic hindrance) in PMMA. The degree of amorphousness decreases up to 140 °C for PMMA and PMACl, beyond which it starts to increase. This is indicative of the improved alignment of macro molecular chains upon heating only up to 140 °C.
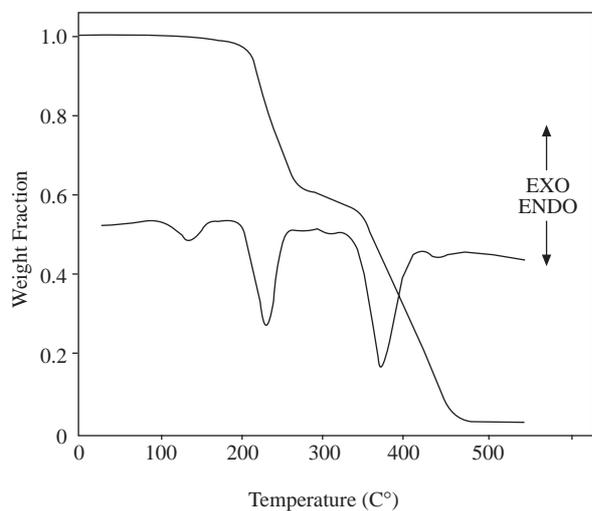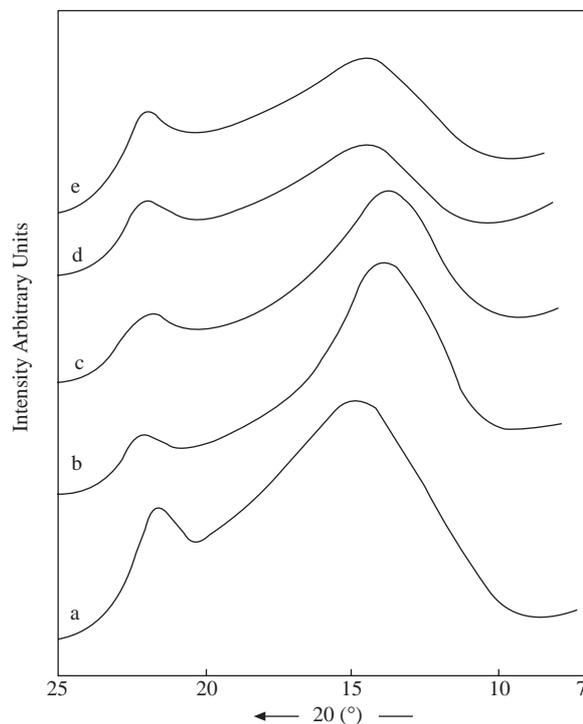

Figure 1. TG and DTA curves of PMMA.
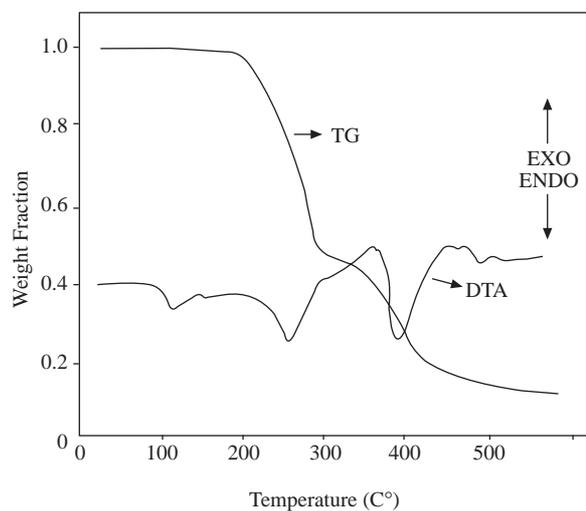
Figure 2. TG and DTA curves of PMACl.
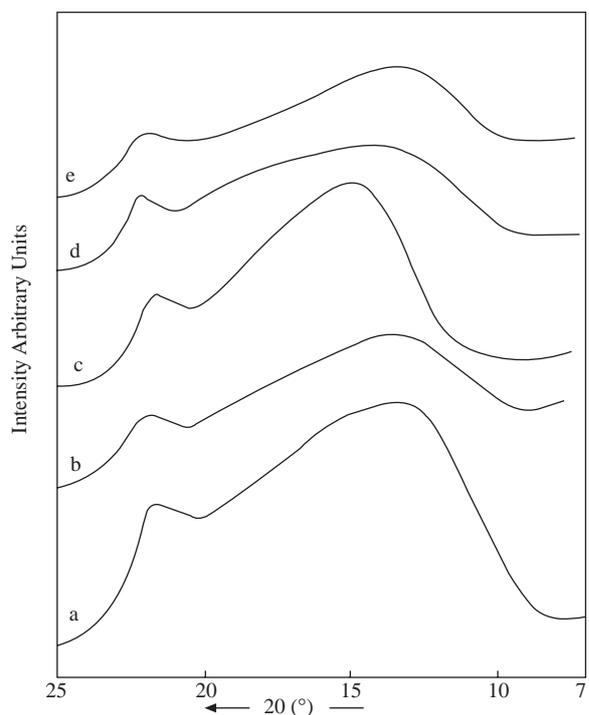
Figure 3. X-ray diffractograms of PMMA heated at A = 25 °C, b = 90 °C, c = 140 °C, d = 220 °C & e = 410 °C.

Figure 4. X-ray diffractograms of PMACl heated at A = 25 °C, b = 90 °C, c = 140 °C, d = 220 °C & e = 410 °C.

Table

Parameter	Poly (methyl methacrylate)					Poly (methacryloyl chloride)				
	25 °C	90 °C	140 °C	220 °C	410 °C	25 °C	90 °C	140 °C	220 °C	410 °C
D.O.A.	9.65	6.65	6.80	9.00	9.35	7.00	4.45	4.85	6.45	7.15
R (°A)	8.05	8.05	7.38	7.91	8.24	7.95	8.05	8.05	7.51	7.77
Lc (°A)	8.02	11.64	11.39	8.61	8.28	11.07	14.40	13.64	12.02	10.91

where D.O.A. = Degree of amorphousness
R = Interchain separation
Lc = Degree of order or mean crystallite size

The interchain separation (R) can be measured by the value of 2θ at which the intensity of the diffuse halo is maximum using the equation

$$R = 5/8 \; (\lambda/\sin\theta)$$

The results presented in Table show that the interchain separations do not differ much.

The X-ray diffractograms of polymers seldom show the sharpness associated with inorganic and organic crystals, because the polymer crystals are small or imperfect. Hence, the descriptive term used for these is "crystallite". The degree of order in polymers is determined from the measurement of the crystallite size. The mean crystallite size (Lc) was calculated by the method of Short and Walker [13]

$$Lc = 57.3 \; K\lambda/\beta \; \cos\theta$$

where K = Scherrer's constant (0.87), λ = wavelength of X-rays (1.5418°A), β = peak width at half height (2θ). The data in Table show that the Lc values for PMMA increase up to 140 °C, after which they decrease. It is an established fact that in polymers the randomness of polymeric coils is increased at melting temperatures, beyond which degradation starts [14]. Similar phenomena are discernible for PMACl samples, when the polymer starts to degrade, as beyond the melting temperatures the degree of order decreases.

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