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THERMAL STABILITY OF POLY(ACRYLOYL CHLORIDE) HOMOPOLYMER AND COPOLYMERS OF ACRYLOYL CHLORIDE WITH METHYL METHACRYLATE

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The thermal stabilities of poly(acryloyl chloride) homopolymer and copolymers of acryloyl chloride with methyl methacrylate covering the entire composition range were studied by thermogravimetric analysis. At each extreme of the composition range incorporation of comonomer units results in a copolymer which is less stable than the PMMA homopolymer. The activation energies of the decomposition of the copolymers were calculated using the Arrhenius equation and found to decrease from 32.2 to 12.5 kJ mol^{-1} as acryloyl chloride concentration of the copolymer increases, indicating that the copolymers of higher acryloyl chloride concentration should easier decompose than other copolymers. The reactivity ratios of the copolymer were calculated and found to be $r_1(\mathrm{AC}) = 0.2 \pm 0.02$ and $r_2(\mathrm{MMA}) = 0.9 \pm 0.1$.

The noninflammability properties of halogenated polymeric materials have been given a great deal of attention in the last few years [1, 2], their properties of decomposition and thermal stability have been of particular interest [3, 4]. In the last few years we were concerned with brominated homopolymers and copolymers [5–7]. Zazhalilov et al. [8] studied the stability of copolymers of methacryloyl chloride with methyl methacrylate and found that the stability of the copolymers were improved by reaction with the sodium salt of 2-mercaptobenzothiazole. In the present investigation we report the thermal stability of poly(acryloyl chloride) homopolymer and copolymers of acryloyl chloride with methyl methacrylate.

Experimental

Materials

a) Acrylic acid and methyl methacrylate (BDH Chemical Ltd) were distilled under nitrogen, fractions between 139–140° and 100–100.5° respectively were collected. This procedure removed both inhibitor and impurities.

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b) Benzoyl chloride (M & B Laboratory Chemicals).

c) Acryloyl chloride (AC): Thoroughly mix 300 g of acrylic acid and 1000 g of benzoyl chloride in a three necked 2 l round-bottomed flask equipped with a mechanical stirrer, a 20 cm Vigreux column plus distilling head, and nitrogen bubbler. Distill with stirring under N_2 atmosphere, and collect all product distilling below 80° in an ice-cooled receiver containing about 0.5 g of hydroquinone. The yield of crude acryloyl chloride is 290 g (73%). Redistill the acryloyl chloride, and collect the fraction boiling between 74 and 79° in an ice-cooled receiver containing 0.5 g of hydroquinone to obtain 250 g (66%) of pure acryloyl chloride. Store at 0° in a tightly glass-stoppered flask.

d) Purification of initiator: 2,2'-Azobisisobutyronitrile (AIBN) (Eastman Kodak) was used as an initiator (0.1 *w/v*) for all polymerizations. It was purified by dissolving in hot ethanol [9] and filtering. The solution was left to cool, the pure material was collcted by filtration and kept under vacuum.

e) Preparation of the polymers: PAC, PMMA homopolymers and AC–MMA copolymers were prepared by free radical initiation using AIBN as an initiator and anhydrous ethyl acetate (50/50 *v/v*) as solvent under vacuum at 60 ± 0.02° to about 10% conversion. They were then precipitated in petroleum ether (b.p. 40–60°). Four different compositions of the copolymers, with 10, 26, 35 and 62 mol % AC units, were prepared to determine the reactivity ratios. Molecular weights were determined by osmometry in toluene or in cyclohexane. PAC and PMMA had $\overline{M}_n$ values of 356,000, respectively, and those of the copolymers were 150,000, 102,000, 78,000 and 56,000, with 10, 26, 35 and 62 mol % AC units, respectively.

Analytical techniques

a) Microanalysis: Chlorine contents of the copolymers were determined in the Microanalytical Unit in Cairo University. The average of five values of chlorine contents were obtained for each sample and the average were used for the determination of the copolymer composition.

b) Thermal method of analysis: Thermogravimetry: TG measurements were made in a dynamic nitrogen atmosphere, 70 ml/min, on the DuPont thermobalance using 5 mg samples and a heating rate of 10 deg/min. The boat-shaped sample holder was of platinum approximately 12 mm long and 3 mm deep. Differential thermal analysis: A DuPont 950 instrument was used to obtain DTA curves with small glass beads as reference. The sample was heated at 10 deg/min from ambient temperature to 500° in a nitrogen flow (80 ml/min).

Results and discussion

Determination of reactivity ratios of AC–MMA copolymers

The average of give values of chlorine percentages of each sample was used for the calculation of copolymer composition. By knowing the number of moles of the monomer mixture and the molar ratio in the copolymer, reactivity ratios were calculated using the equation [10]:

$$\frac{f_1(1-2F_1)}{(1-f_1)F_1} = \frac{f_1^2(F_1-1)}{(1-f_1)^2F_1}r_1 + r_2$$

where $F_1 = \frac{M_1/M_2}{M_1/M_2+1}$ is the mole fraction of AC (M_1) in the polymer, $f_1 = \frac{n_1}{n_1+n_2}$ is the mole fraction of M_1 in feed, and r_1 and r_2 are the reactivity ratios for AC and MMA, respectively. Figure 1 represents a plot of $\frac{f_1(1-2F_1)}{(1-f_1)F_1}$ versus $\frac{f_1^2(F_1-1)}{(1-f_1)^2F_1}$ and Fig. 2 is a plot of $\frac{f_2(1-2F_2)}{(1-f_2)F_2}$ versus $\frac{f_2^2(F_2-1)}{(1-f_2)^2F_2}$, where $F_2 = \frac{M_2/M_1}{M_2/M_1+1}$ is the mole fraction of MMA (M_2) in polymer and $f_2 = \frac{n_2}{n_1+n_2}$ is the mole fraction of M_2 in feed. From the slopes and intercepts reactivity ratio values for AC–MMA copolymer are $r_1(\mathrm{AC}) = 0.1 \pm 0.02$ and $r_2(\mathrm{MMA}) = 0.9 \pm 0.1$.

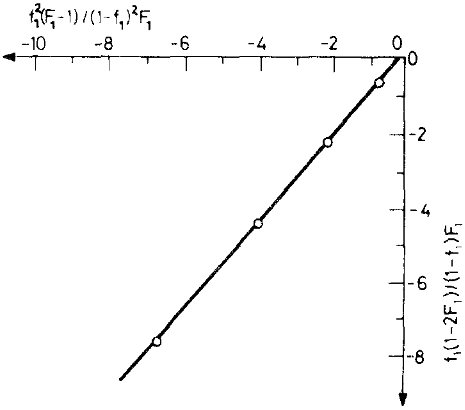

Fig. 1 Graph of $f_1^2(F_1-1)/(1-f_1)^2F_1$ vs. $f_1(1-2F_1)/(1-f_1)F_1$ for AC–MMA copolymers.

Thermal analysis of PAC and PMMA homopolymers and copolymers of AC–MMA

DTA traces of the homopolymers and copolymers are illustrated in Fig. 3. Two endothermic peaks are clearly visible, their relative importance being dependent upon the copolymer composition. The T_{max} for each peak is shown on the traces, which are comparable to those of the corresponding polymers.

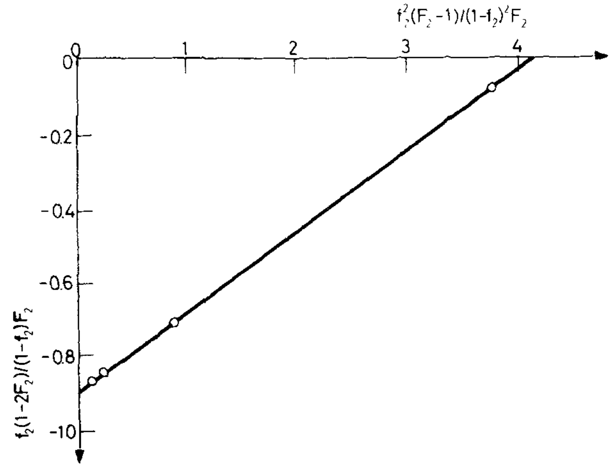

Fig. 2 Graph of $f_2^2(F_2-1)/(1-f_2)^2F_1$ *vs.* $f_2(1-2F_2)/(1-f_2)F_2$ for AC–MMA copolymers.

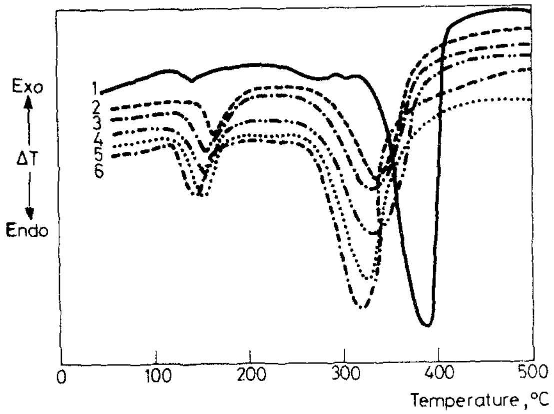

Fig. 3 3 DTA curves for PAC, PMMA and AC–MMA copolymers. 1: PMMA, 2: 10% AC, 3: 26% AC, 4: 35% AC, 5: 62% AC, 6: PAC

TG curves of PAC, PMMA homopolymers and AC–MMA copolymers are shown in Fig. 4. The degradation starts at ~100° for PAC and ~200° for PMMA. Table 1 presents the percentage weight losses for each polymer and the maximum rate of weight loss shown by the derivative equipment associated with the TG

Table 1 Weight-loss percentage for the homopolymers of PAC and PMMA and AC–MMA copolymers

Polymer mole, % AC	Volatilisation temperature, °C	First stage		Second stage		Wt.% remaining at 500 °C
		T_{max}, °C	wt. loss, %	T_{max}, °C	wt. loss, %	
PAC	105	145	18	320	60	22
62	115	155	20	325	68	12
35	125	160	18	328	79	3
26	135	160	17	330	78	5
10	150	170	15	340	83	2
PMMA	200	270	20	395	78	2

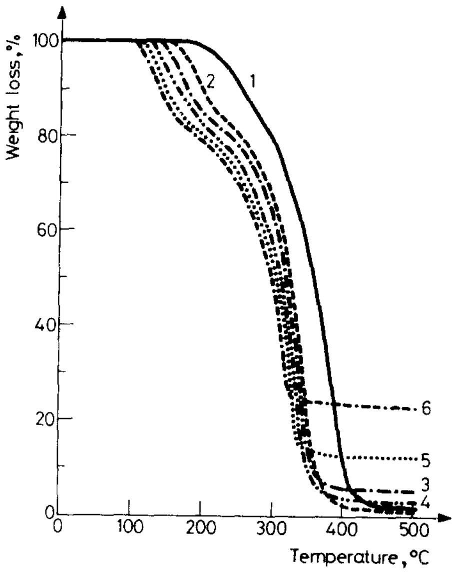

Fig. 4 TG curves for PAC, PMMA and Ac–MMA copolymers. 1: PMMA, 2: 10% AC, 3: 26% AC, 4: 35% AC, 5: 62% AC, 6: PAC

apparatus. All the curves exhibit two-stage degradation behaviour. The TG curves reveal that the stabilities of the copolymers are intermediate between those of the two homopolymers.

To illustrate the initial stages of breakdown more clearly, the degradation was studied at a heating rate of 5 deg/min to give a clear picture on the relative stability of the entire composition range. Smooth changes in stability with composition is well demonstrated in Fig. 5, in which the weight loss percentage at a selected temperature (200°) in the programmed degradation using the data in Fig. 4 is plotted against composition. The most clearly defined feature of the reaction is the increase of stability towards PMMA. This is not the case in the thermal stabilities of vinyl bromide-methyl acrylate and β-bromostyrene-methyl methacrylate copolymers [5, 11], which have stable copolymers at definite compositions.

The effective activation energies of the thermal degradation of PAC, PMMA and copolymers of AC–MMA were determined from the temperature dependence of the initial chain rupture rate. The rate constant of the thermal degradation of PAC and PMMA homopolymers and AC–MMA copolymers were plotted (Fig. 6) and according to Arrhenius' relationship, the activation energies were determined and listed in Table 2. The results in Table 2 show that the activation energies decrease

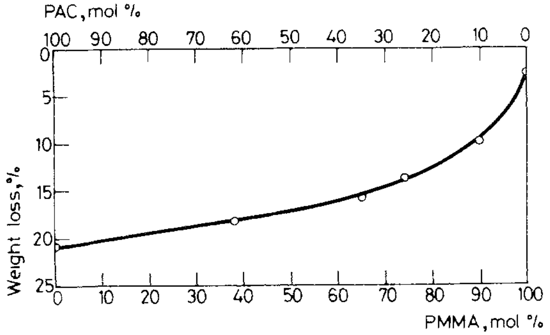

Fig. 5 Comparison of weight-loss percentage at 200 °C with copolymer composition for heating rate 5 deg/min

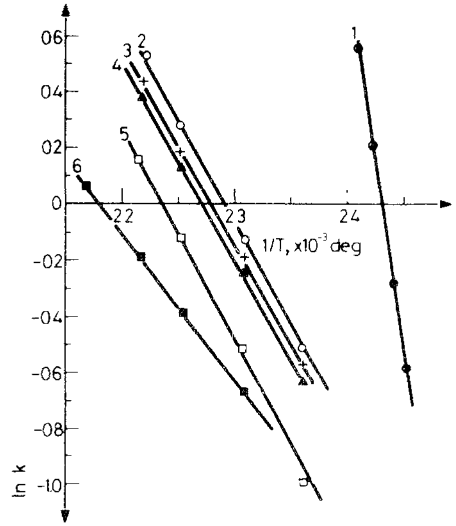

Fig. 6 Arrhenius plot of the rate constant of PAC and PMMA homopolymers and AC–MMA copolymers. 1: PMMA, 2: 10% AC, 3: 26% AC, 4: 35% AC, 5: 62% AC, 6: PAC

from 32.2 to 12.5 kJ/mol as AC concentration in the copolymer increases, indicating that the copolymers with higher concentration of AC should undergoes to decomposition more than the other copolymers.

Table 2 Activation energies of the thermal degradation of PAC and PMMA homopolymers and copolymers of AC with MMA

Polymer	Activation energy, E_a, kJ mol^{-1}
PAC	10.5
62% AC	12.5
35% AC	25.1
26%AC	27.2
10% AC	32.2
PMMA	112.9

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Zusammenfassung — Mittels thermogravimetrischer Untersuchungen wurde die thermische Stabilität des Polypropenoylchloridhomopolymers und von Kopolymeren von Propenoylchlorid mit Methylmetacrylat im gesamten Mischungsbereich untersucht. Bei jedem Extremwert im Mischungsbereich resultiert der Einbau von Komonomereinheiten in einem Kopolymer, das instabiler als das PMMA Homopolymer ist. Die Aktivierungsenergien für die Zersetzung der Kopolymere wurden mittels der Arrheniuschen Gleichung errechnet und sinken bei abnehmender Konzentration des Propenoylchlorides im Kopolymer von 32,2 auf 12,5 kJ/mol ab. Dies zeigt, daß Kopolymere höherer Propenoylchloridkonzentration sich leichter zersetzen als andere Kopolymere. Die Reaktivitätsquotienten der Kopolymere wurden mit r_1(AC) = 0.2±0.02 und r_2(MMA) = 0.9±0.1 errechnet.

Резюме — С помощью термогравиметрического анализа исследованы термоутойчивости гомополимера полиакрилоилхлорида и сополимеров акрилоилхлорида с метилметакрилатом во всей области их состава. В каждой экстремальной области состава происходит внедрение комономерных звеньев в сополимер, вследствии чего он менее устойчив, чем гомополимер полиметилметакрилат. На основе уравнения Аррениуса были вычислены энергии активации разложения, которые при увеличении концентрации акрилоилхлорида уменьшались от 32,2 до 12,5 кдж·моль$^{-1}$, указывая тем самым на более легкое разложение сополимеров с более высокой концентрацией акрилоилхлорида. Соотношения реакционных способностей для сополимера акрилоилхлорида были равными $r_1 = 0{,}2 \pm 0{,}02$, а для метилметакрилата $r_2 = 0{,}9 \pm 0{,}1$.