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Thermal degradation behavior of radiation synthesized polydiallyldimethylammonium chloride

Sanju Francis *, Lalit Varshney, Sunil Sabharwal

Radiation Technology Development Section, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

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Abstract

Thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) studies were carried out on gamma radiation synthesized polydiallyldimethylammonium chloride (PDADMAC). The polymer was found to undergo thermal degradation in two stages. The first stage showed a weight loss of 33% and the second stage showed a weight loss of 67%. The DSC thermogram shows two endothermic peaks corresponding to the two stages in the TG thermogram and the experimental enthalpy change associated with the first and second stages were 650 J g^{-1} and 129.5 J g^{-1}, respectively. The *n*th-order kinetic parameters (order of the reaction, activation energy and the pre-exponential factor) were determined from a single dynamic DSC or thermogravimetric (TG) thermogram by the method of least square. Theoretical TG/differential thermogravimetric (DTG) and DSC thermograms derived from the calculated kinetic parameters were in good agreement with the experimental ones at the heating rate employed. However, the kinetic parameters determined using TG and DSC were different. This leads to the conclusion that the degradation mechanism could be complicated and may consists of a number of parallel or consecutive reactions. The glass transition temperature (T_g) of the polymer was found to be around 150 °C depending on the test method employed.

Keywords: Gamma radiation; Polydiallydimethylammonium chloride; DSC; TGA; Kinetics

1. Introduction

In recent years, polyelectrolytes have been subject of increased research efforts due to their versatile commercial applications. Among the water soluble cationic ammonium monomers, diallyldimethylammonium chloride (DADMAC) and its homopolymer poly (diallyldimethylammonium chloride) (PDADMAC) and its copolymers with other monomers has found lot of commercial utility. PDADMAC is useful in water treatment as flocculants and coagulants [1–4], for the removal of organic and mineral contaminants such as arsenic, ultrafiltration aids and water clarification. It is used in the textile and paper industries for making antibacterial fiber and as an additive to improve the wet strength of papers. It also finds applications in cosmetic and personal care industries; in biology, medicine, and food applications; and in membrane technology [5].

To the best of our knowledge, no detailed thermal investigations have been carried out on PDADMAC.

* Corresponding author.
E-mail address: sanju@barc.gov.in (S. Francis).

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Some applications of the polymer may require its use at high temperature. The thermal stability of a polymer is related to the initial degradation temperature (onset) and also the rate of degradation of polymer. The determination of kinetic parameters associated with the degradation has a lot of practical significance as the evaluation of the parameters helps in predicting the thermal behavior of polymer. The objective of the present study is to evaluate the kinetic parameters (order of the reaction, activation energy and the pre-exponential factor) of PDADMAC degradation from a single TG or DSC scan using the method of least squares.

2. Experimental

2.1. Materials

2.2. Polymer used and its characterstics

PDADMAC was synthesized by gamma irradiation of DADMAC monomer solution (3 M) to varying doses (5–27 kilogray). The yield of the polymer was determined gravimetrically and was found to vary from 30% to 90% depending on the irradiation dose. ^{13}C-NMR, H-NMR and FT-IR analyses confirmed that the polymer was formed almost exclusively by the cyclopolymerization [6–8] of the monomer and did not contain any residual allylic groups. The molecular weight of the samples was determined viscometrically using Mark–Houwink–Sakurada relation [9] and was found to be in the range 2.5×10^4 to 4.6×10^4. Preliminary investigations revealed that the thermal decomposition profiles (DSC and TGA) of the polymer samples (in powder form) of different molecular weights were similar. Therefore, PDADMAC synthesized at a radiation dose of 27 kGy ($M_v = 4.6 \times 10^4$) was used for all subsequent experiments reported herein.

2.3. Thermogravimetric analysis (TGA)

The non-isothermal thermogravimetric (TG) measurements were carried out with Mettler thermogravimetric analyzer (TG 50) coupled with a Mettler TC 10A processor. The temperature calibrations were carried according instrument manual [10]. The calibration method was based on the change in magnetic properties of three metal samples (Alumel, Nickel and Trafoperm) at their curie temperatures. The experimental data collected were transferred to a computer and kinetic analyses were carried out by Mettler STAR^e program [11]. Approximately 15 mg of the polymer samples were taken in an open alumina crucible and the degradation profiles were recorded from 35 °C to 800 °C at a heating rate of 10 °C min^{-1}. The decomposition was carried out in an inert dynamic atmosphere of high purity nitrogen set at a flow rate of 50 ml min^{-1}.

2.4. Differential scanning calorimetry (DSC)

Thermoanalytical thermograms were recorded using Mettler-Toledo DSC 823e with liquid nitrogen cooling assembly. The heat flow and temperature calibrations were carried according to the instrument manual [11]. All the experiments were carried out in an inert dynamic atmosphere of high purity nitrogen set at a flow rate of 50 ml min^{-1}. About 5 mg of the powdered polymer samples were taken in a standard 40 μl aluminum pan. Since the polymer samples were highly hygroscopic in nature, the thermal properties were determined using two scans. The first scan was carried out to eliminate the residual water from the polymer samples. In the first scan the sample was heated from 40 °C to 200 °C at 20 °C min^{-1} rate, kept isothermally at 200 °C for 10 min and cooled to 0 °C at 10 °C min^{-1} rate. For the determination of glass transition temperature, the second scan was performed from 0 °C to 500 °C at a higher heating rate of 50 °C min^{-1}. The second scan was performed from 0 °C to 500 °C at a heating rate of 10 °C min^{-1} for evaluating the Arrhenius parameters. For convenience, only the second scan is shown in the figures. Both TGA and DSC baselines were corrected by subtraction of a prerecorded blank thermogram.

2.5. Kinetic analysis

Thermogravimetric analysis (TGA) as a thermal analysis technique, measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere. TGA measurements are used primarily to determine the composition of materials and to predict their thermal stability under elevated temperatures. The weight loss data supplied by the thermogravimetric measurement is completely unspecific and gives no information about the nature of the degradation products. This type of information is only obtained when a TGA instrument is connected via a suitable interface to a device capable of analyzing gases. However, with proper experimental procedures,

additional information about the kinetics of decomposition can be obtained from TGA and DSC.

The thermal decomposition of a solid is usually a complex process but can be approximated by the rate equation:

$$A_{\text{solid}} \rightarrow B_{\text{solid}} + C_{\text{gas}} \tag{1}$$

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{2}$$

where $k(T)$ is a function of temperature and $f(\alpha)$ is a function of conversion. When the nth-order model equation is combined with the Arrhenius equation the reaction rate is given:

$$\frac{d\alpha}{dt} = k\exp(-E_a/RT)\cdot(1-\alpha)^n \tag{3}$$

where $d\alpha/dt$ is the rate of reaction, T is the sample temperature, k is the pre-exponential factor, α is the conversion of the reaction, E_a is the activation energy, n is the order of the reaction and R is the universal gas constant.

To obtain $d\alpha/dt$ and α from DSC and TGA, the following equations can be used:

$$\text{DSC:} \quad \frac{d\alpha}{dt} = \frac{H}{A_{\text{tot}}} \tag{4}$$

H: DSC signal from baseline (mW), A_{tot}: Total peak area (mJ), α: Partial area (mJ)/total peak area (mJ).

$$\text{TGA:} \quad \frac{d\alpha}{dt} = \text{DTG signal } (\text{mg}^{-1})/\text{total weight stage(mg)} \tag{5}$$

α = Partial weight stage (mg)/total weight stage (mg).

There are various methods for the determination of kinetic parameters by thermal analysis depending on the assumptions and approximations involved. Kissinger's method (standard ASTM E 698) [12,13], Freeman and Carroll (differential method) [14], Coats and Redfern (integral method) [15], etc. are some of the commonly used methods. Another popular and frequently used method for determination of the kinetic parameters is non-linear regression [16]. Ideally, the kinetic parameters evaluated from multiple TG measurements are closer to the actual values for a particular reaction, but the determination is inconvenient and time consuming. In the present study, nth-order kinetic parameters were determined from a single dynamic TG thermogram and from a single DSC thermogram. Sets of three values T, $d\alpha/dt$ and α were taken from the dynamic DSC or TGA thermogram and k, E_a and n were then calculated by the method of least squares. DSC and TG scans were performed in triplicate and the average values of the parameters are reported in this study.

3. Results and discussion

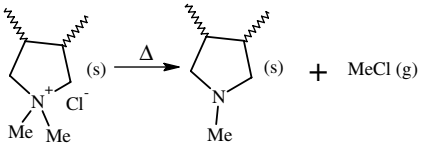
3.1. TG and DTG analysis

Fig. 1 shows the TG and DTG thermograms of PDADMAC recorded at a heating rate of 10 °C min^{-1}. Three well defined and resolved stages are seen in the figure. The initial stage (shown as stage 0 in the figure) from 35 °C to around 120 °C is due to the loss of moisture from the polymer sample. This was confirmed from the DSC scan, where an endothermic peak appeared (onset at ~0 °C) due to the freezing of residual moisture in the sample. Stage I and stage II in the figure corresponds to the actual polymer degradation. In stage I, the polymer starts decomposing and the decomposition takes place over a broad temperature range of 287 °C (onset) and 355 °C (endset). The maximum rate of weight loss was found to be 320 °C from the DTG thermogram.

The thermal properties of simple quaternary ammonium salts have been investigated by several workers [17–22]. It was initially suggested and later confirmed that quaternary ammonium salts dissociate with the formation of alkyl halide.

$$[NR_4]X \rightarrow NR_3 + RX \tag{6}$$

where X and R indicates a halogen atom and an alkyl or aryl substituent, respectively. By analogy, we can expect PDADMAC to undergo a similar reaction as shown below.



(7)

PDADMAC

Mw = 161.68 Mw = 111.18 Mw = 50.5

Theoretically, the weight loss for the above reaction is 31.24% and the experimental TG thermogram shows a weight loss (%) of 33.0 ± 2.0 for the first stage. This value corresponds well with the theoretical value and the degradation mechanism of the first stage could be revealed from Eq. (7). The stage II degradation takes place over a relatively narrow

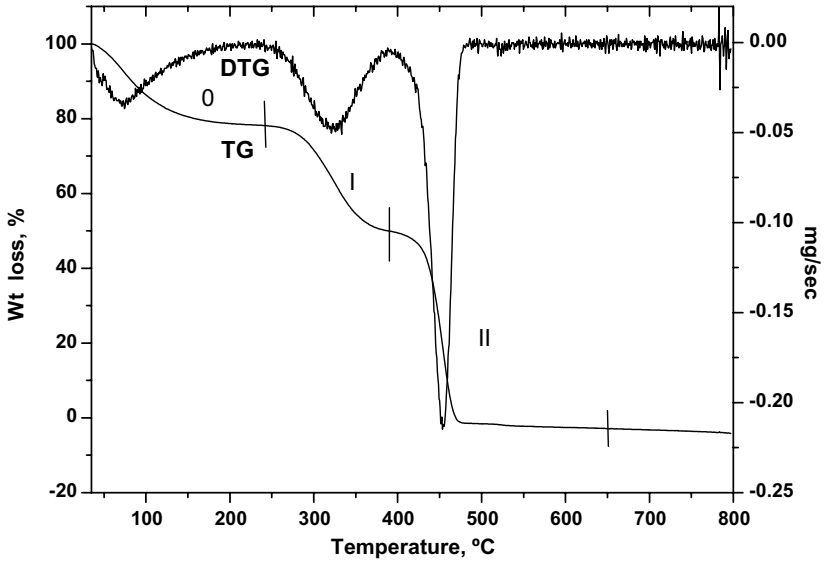


Fig. 1. TG and DTG thermogram of PDADMAC in nitrogen atmosphere at a heating rate of 10 °C min^{-1}.

temperature region between 435 °C (onset) and 467 °C (endset) with the DTG peak at 453 °C. The weight loss (%) for Stage II was found to be 67.0 ± 2.0. The mechanistic details of the decomposition stages can only be obtained when the thermal analysis technique is coupled with other techniques where the evolved gases and/or the residues are characterized (mass spectrometry, FT-IR, NMR, etc.).

3.2. DSC evaluation

DSC is commonly used to determine the glass transition temperature (T_g) of a polymer. The glass transition is a kinetic phenomenon and is dependent on how the measurement is made. T_g mainly depends on the thermal history of the sample and also on the heating/cooling rate. The higher the heating rate, the higher is the DSC sensitivity. Hence, for the determination of weak glass transition, a fast heating rate of 50 °C min^{-1} was preferred. On the contrary, for higher resolution of the peaks and for kinetic parameter calculations, a lower heating rate of 10 °C min^{-1} was employed. Figs. 2 and 3 show the DSC scan of the sample at the heating rate of 10 °C min^{-1}. The DSC thermogram shows two endothermic peaks corresponding to the two stages in the TG thermogram. From Table 2, it can be seen that the enthalpy change associated with the first stage (ΔH_I) is 650 J g^{-1}. The second degradation stage had an enthalpy change (ΔH_{II}) of 129 J g^{-1}. Fig. 3 inset shows the DSC scan at a heating rate of 50 °C min^{-1}. For the determination of the glass transition temperature of a polymer, there are different standard evaluation procedures like ASTM [23], DIN [24] and Richardson's method [25]. The glass transition temperature and Δc_p (specific heat capacity) obtained through different methods by the Mettler STAR^e program is shown in Table 3. The ASTM and DIN gave close results (around 150 °C), however the Richardson method revealed a higher value of about 165 °C. At the lower heating rate (10 °C min^{-1}), the glass transition is further resolved into many transitions (α, β, γ, etc.).

3.3. Comparison of TG and DSC results

Fig. 2 shows the DTG plot along with the DSC thermogram scanned at the same heating rate of 10 °C min^{-1}. From the figure, it can be seen that there is an almost one to one correspondence in the peaks of DTG and DSC. Comparing DTG and DSC data from Tables 1 and 2, it can be seen that the peak temperatures of the DSC thermogram have higher values (329 °C and 461 °C) than the corresponding DTG thermogram (320 °C and 453 °C). Another interesting observation is that the enthalpy change (DSC) associated with the first stage (650 J g^{-1}) is considerably higher than that associated with the second stage (129 J g^{-1}) though the weight loss (TGA) in the first stage is only 33% of the total weight loss. The kinetic parameters, acti-

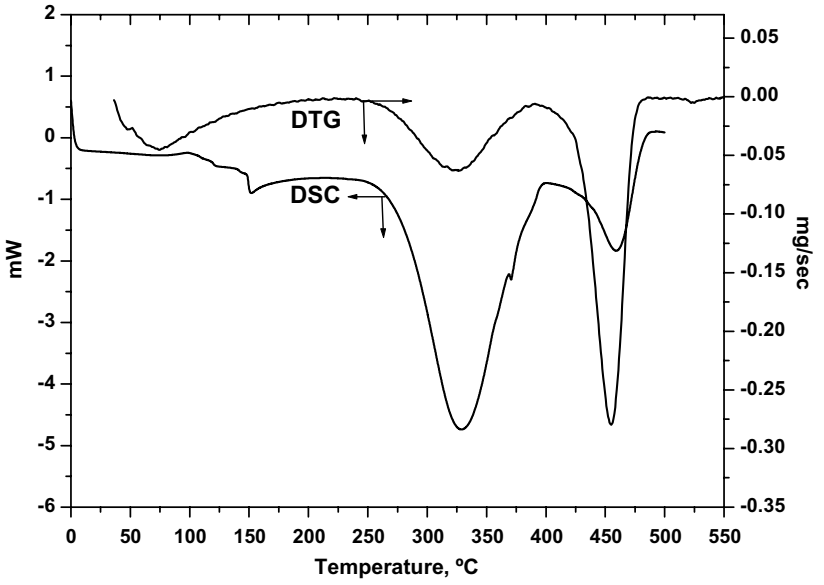


Fig. 2. DSC and DTG thermogram of PDADMAC in nitrogen atmosphere at a heating rate of 10 °C min^{-1}.

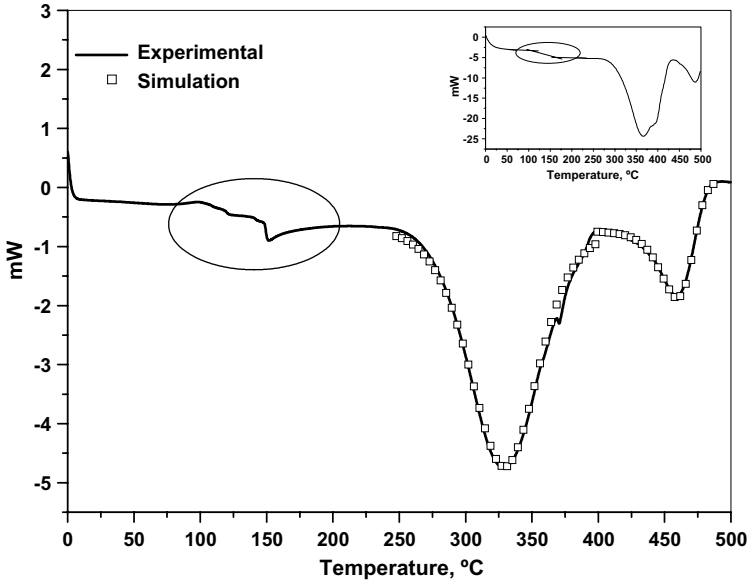


Fig. 3. Comparison of experimental DSC thermogram (10 °C min^{-1}) with theoretically generated thermogram by the method of least squares. Inset: DSC thermogram recorded at heating rate of 50 °C min^{-1} for determination of glass transition.

Table 1
TG/DTG analysis of PDADMAC at a heating rate of 10 °C min^{-1} in nitrogen atmosphere

	Step I	Step II
Step range (°C)	223 – 391	391 – 730
Weight loss (%)	33 ± 2.0	67 ± 2.0
Onset temp (°C)	287	435
Endset temp (°C)	355	467
DTG peak (°C)	320.7 ± 0.4	453.2 ± 0.3

Table 2
DSC analysis of PDADMAC at a heating rate of 10 °C min^{-1} in nitrogen atmosphere

	Step I	Step II
Onset temp (°C)	275	435
Endset temp (°C)	349	482
ΔH (J g^{-1})	650.2 ± 40.3	129.5 ± 10.7
DSC peak (°C)	329.4 ± 0.2	461.7 ± 0.6

vation energy, lnk and order of the reaction, calculated from the DSC and TG thermograms are shown in Table 4. The degree of conversion α was in the range 0.1–0.9 for the evaluation. The Arrhenius parameters derived from the DSC measurements are higher than those from the TG measurements for the first degradation stages. On the other hand, for the second degradation stage, the TG analysis yields a higher value for the parameters than the DSC calculations.

Table 3
Evaluation of glass transition temperature of PDADMAC by different methods

	ASTM	DIN	RICHARDSON
T_g (Midpoint)	150.05	148.41	165.85
Δc_p (J g^{-1} K^{-1})	0.411	0.586	0.352

Table 4
Evaluation of kinetic parameters from TGA and DSC using the method of least squares

Method	Step I		Step II	
	TGA	DSC	TGA	DSC
lnk	19.6 ± 2.1	25.2 ± 2.3	67.4 ± 5.4	38.4 ± 3.8
E_a (kJ/mol)	122.1 ± 8.6	150.4 ± 7.2	432.6 ± 15.1	262.6 ± 11.2
n	1.5 ± 0.1	1.7 ± 0.2	1.3 ± 0.1	0.68 ± 0.1
R^2	0.9986	0.9885	0.9967	0.9893

3.4. TG and DSC simulation

The Mettler STAR^e software enables one to fit or simulate the experimental thermogram over the α range chosen using the method of non-linear regression. The actual verification for any kinetic results is to compare the experimental TGA/DTG or DSC thermogram with the theoretically generated thermogram based on any particular model. The shape of the fit is strongly dependent on the pre-exponential factor in the Arrehenius equation although its physical meaning is not clear for a complex degradation mechanism. However, emphasis is usually given to the determination of the activation energy for the decomposition. The quality of the thermogram fit is expressed by the R^2 values from the least square analysis method. It can be seen from the Figs. 3 and 4 and Table 4 (R^2 values) that the agreement between the simulated DSC/DTG thermogram and the experimental thermograms is good. But, as mentioned earlier, the kinetic parameters derived from the DSC and TG is significantly different. If the degradation process takes place in a single stage then the weight loss (TGA) and the enthalpy change (DSC) is directly related to the extent of reaction. Since the TGA and DSC results are different in the present study, the degradation process of the PDADMAC could be complicated and may involve a number of reactions or stages. The TG measurement would follow only the weight loss

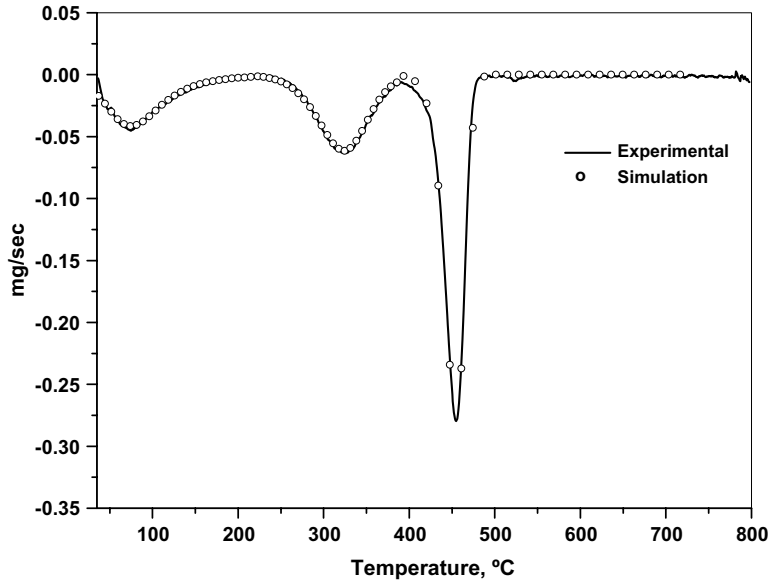


Fig. 4. Comparison of experimental DTG thermogram with theoretically generated thermogram by the method of least squares.

associated with the decomposition of the intermediates. The DSC, on the other hand, would follow the weighted sum of the decomposition of the intermediates depending on the change in enthalpy for each stage [26]. In such cases the course of the reaction followed by the TGA and DSC would be different.

4. Conclusions

A kinetic study on the thermal degradation of polydiallyldimethylammonium chloride was carried out. TGA and DSC show that the degradation is a two stage process. The kinetic triplet (order of the reaction, activation energy and the pre-exponential factor) was determined from a single TG measurement and also from a single DSC thermogram using the method of least square. A theoretical thermogram (simulation) was generated on the basis of the kinetic parameters calculated and compared with the experimental thermogram, to verify the results obtained. The agreement between the simulated DSC/TG thermogram and the experimental DSC/TG thermograms was good. But, the kinetic parameters derived from the DSC were significantly different from the parameters derived from TGA. From all the above, the degradation process of the PDADMAC may be complicated involving a number of consecutive or parallel reactions. Since TG measures the loss of sample weight due to thermal degradation, it is a direct technique and gives more reliable information on the degradation kinetics than DSC.

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