

Thermogravimetric Approach for Determining the Degree of Conversion in Radiation-Polymerized DADMAC

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ABSTRACT: The degree of conversion of the monomer diallyldimethylammonium chloride (DADMAC) to its polymer, poly(DADMAC), was determined using dynamic thermogravimetry (TG). DADMAC solution was exposed to different radiation doses, and the degree of conversion of the monomer to the polymer was determined from a calibration plot generated previously from solutions containing known monomer–polymer ratios. The concentration of monomer and polymer in the mixture was estimated by measuring the weight loss corresponding to the steps involved in the thermograms. By employing the method, polymerization of

DADMAC as a function of irradiation dose was studied. The degree of conversion of DADMAC increases considerably during the initial stages of irradiation, up to a dose of 40 kGy, after which the increase in conversion is not very significant. To validate the method, the degree of conversion was also determined by classical gravimetry, and the results were found to be in good agreement. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 668–672, 2009

Key words: diallyldimethylammonium chloride; TGA; degree of conversion; radiation

INTRODUCTION

Diallyldimethylammonium chloride (DADMAC) is a water-soluble cationic ammonium monomer that undergoes cyclopolymerization to yield its polymer, poly(DADMAC), which finds a lot of commercial utility.^{1–5} Although poly(DADMAC) is one of the most commercially important quaternary ammonium polymers, not many methods have been reported for determining the degree of conversion in DADMAC polymerization. This may be because of the experimental difficulty in handling the highly hygroscopic monomer or polymer. Nevertheless, the degree of conversion of DADMAC is usually studied by classical gravimetry or by using the ¹H NMR technique.⁶ In gravimetry, the polymer is precipitated by adding a nonsolvent, preferably acetone or isopropanol and the polymer is separated, dried, and weighed. This method is time consuming and prone to experimental error. In ¹H NMR, the allylic proton signal is monitored. As polymerization proceeds, the proton signal intensity decreases because the double bond is consumed in the polymerization reaction. The intense peak due to H₂O proton interferes with the intensity measurement of the allylic proton. Hence, D₂O should be used as the solvent instead of H₂O. This technique gives accurate and

reproducible results, but it requires expensive instruments and careful sample preparation in D₂O. Also, the rate of polymerization of the monomer may differ in D₂O and H₂O.

In this study, we report a simple and convenient method to determine the degree of conversion of DADMAC to its polymer using dynamic thermogravimetry. The monomer solution, exposed to different radiation dose (different degree of conversion), was removed from the radiation field and thermogravimetric analysis (TGA) runs were taken. The conversion degree of the monomer to the polymer was determined from a calibration plot generated previously using different known monomer–polymer ratios. One of the main advantages of the method is that the concentration of the polymer or monomer could be directly determined without their separation. To our knowledge, no thermal methods have been reported to determine the degree of conversion of DADMAC to poly(DADMAC).

EXPERIMENTAL

Materials

Aqueous DADMAC solution (~ 65%) was purchased from Fluka and used without further purification. The poly(DADMAC) used in the study was synthesized by γ -irradiation of DADMAC solution to a dose of 27 kGy.⁷ The molecular weight of the polymer was determined viscometrically using Mark–Houwink–Sakurada relation and was found to

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be 4.6×10^4 . The molecular weight of poly(DADMAC) depends on the absorbed radiation. However, preliminary investigations revealed that TG profile is not affected by the molecular weight of the polymer in the radiation dose range studied (4–70 kGy).

Gamma irradiation

The monomer was irradiated in a ^{60}Co gamma chamber, GC-5000 (BRIT, India) from 4 to 70 kGy at a dose rate of 3.8 kGy h^{-1} . The dose rate was determined using Fricke dosimeter.

Calibration curve

Stock solutions of DADMAC (43 wt %) and poly(DADMAC) (43 wt %) were prepared separately in water. Ternary solutions of monomer, polymer, and solvent were prepared by mixing the monomer and polymer solutions in appropriate ratios. The compositions of the solutions are given in Table I. The total concentration (monomer + polymer) of the solution remains 43 wt %. TGA was carried out on the mixture, and the percentage weight loss due to the monomer/polymer was determined. A calibration curve was made by plotting the percentage weight loss of DADMAC/poly(DADMAC) as a function of poly(DADMAC) concentration.

Classical gravimetry

The monomer to polymer conversions at the different irradiation doses were also determined by classical gravimetry. The poly(DADMAC) formed on irradiation was precipitated with excess isopropanol. It was further purified by dissolving it in minimum amount of water and reprecipitating with isopropanol many times. The polymer samples were dried in air oven at 70°C till they attained constant weight. The degree of conversion was calculated as follows:

Degree of conversion

$$= \frac{\text{Weight of polymer precipitated}}{\text{Initial weight of monomer}} \quad (1)$$

Thermogravimetric analysis

The dynamic thermogravimetric analyses were carried out with Mettler thermogravimetric analyzer (TG 50) coupled with a Mettler TC 10A processor. The temperature calibrations were carried out according to the instrument manual.⁸ The calibration method is 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

TABLE I
Composition of the Ternary Solution (for 100 g)

| Monomer (g) | Polymer (g) | Monomer + polymer (g) | Water (g) |
|-------------|-------------|-----------------------|-----------|
| 4.7 | 38.3 | 43 | 57 |
| 9.5 | 33.5 | 43 | 57 |
| 11.6 | 31.4 | 43 | 57 |
| 17.2 | 25.8 | 43 | 57 |
| 22.4 | 20.6 | 43 | 57 |
| 25.4 | 17.6 | 43 | 57 |
| 34.8 | 8.2 | 43 | 57 |
| 38.7 | 4.3 | 43 | 57 |

and the analyses were carried out by Mettler STAR^e program.⁹ Approximately 75 mg of the sample was taken in an open alumina crucible and the degradation profiles were recorded from 35 to 800°C at a heating rate of $10^\circ\text{C min}^{-1}$. The decomposition was carried out in an inert dynamic atmosphere of high-purity nitrogen set at a flow rate of 100 mL min^{-1} .

Differential scanning calorimetry

Differential scanning calorimetry (DSC) curves were recorded using Mettler-Toledo DSC 823^e with liquid nitrogen cooling assembly. The heat flow and temperature calibrations were carried according to the instrument manual.⁹ All the experiments were carried out in an inert dynamic atmosphere of high-purity nitrogen set at a flow rate of 100 mL min^{-1} . About 15 mg of the monomer solution was taken in a standard $40\text{-}\mu\text{L}$ aluminum pan. The scan was performed from 0 to 500°C at a heating rate of $10^\circ\text{C min}^{-1}$. Both TGA and DSC baselines were corrected by subtraction of prerecorded blank curves.

RESULTS AND DISCUSSION

DSC results

When a monomer solution is heated, there is possibility for it to undergo polymerization, even in the absence of initiators, depending on its reactivity. For example, vinyl monomers like acrylic acid and acrylamide are known to undergo fast polymerization at elevated temperatures. Allyl monomers, on the contrary, polymerize slowly when compared with their vinyl counterparts.¹⁰ However, to rule out the possibility of DADMAC undergoing thermal polymerization, the DSC scan was recorded. Figure 1 shows the DSC thermogram of DADMAC recorded at a heating rate of $10^\circ\text{C min}^{-1}$. The endothermic peak shown as M1 (centered at 220°C) corresponds to the monomer decomposition. The preceding peak is due to the evaporation of water from the solution. No peaks due to the presence of the polymer were

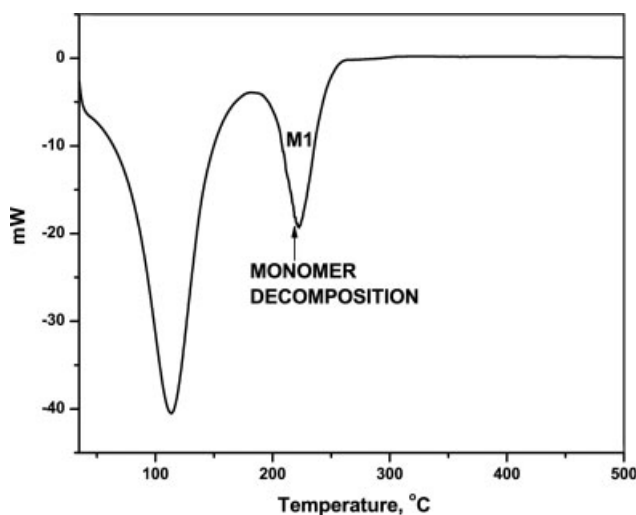


Figure 1 DSC curve of DADM MAC solution in nitrogen atmosphere at a heating rate of $10^{\circ}\text{C min}^{-1}$.

observed in the thermogram of the monomer. Previous DSC studies⁷ have shown that poly(DADM MAC) undergo decomposition in two steps with endothermic peaks centered at 329 and 461°C . This means that heating the monomer solution under the conditions of the experiment does not induce polymerization. This is very important because if the monomer undergoes polymerization during the course of the TGA run, the method is likely to give erroneous results.

TG analyses

Figure 2 shows the TG curves of DADM MAC recorded at a heating rate of $10^{\circ}\text{C min}^{-1}$. The step shown as M1 corresponds to the monomer decomposition. The initial step from 35°C to around 120°C is due to the loss of water from the monomer. In step M1, the monomer decomposition takes place over a broad temperature range from 175 to 247°C . In our previous study,⁷ we investigated the thermal degradation behavior of poly(DADM MAC) and found that the polymer undergoes decomposition in two steps. For clarity, the TG of the polymer (in solution) is also shown in the Figure 2. Steps P1 and P2 in the figure corresponds to the polymer degradation. In Step P1, the polymer decomposition takes place over a broad temperature range from 287 to 355°C . The Step P2 degradation takes place over a relatively narrow temperature region between 435 and 467°C . The weight loss for Steps P1 and P2 were found to be 33 and 67% , respectively (ignoring the step due to water loss). The thermal properties of simple quaternary ammonium salts have been investigated by several workers,^{11–16} and the salts are known to dissociate with the formation of alkyl halide.



where X and R indicates a halogen atom and an alkyl or aryl substituent, respectively. By analogy, we can expect DADM MAC and poly(DADM MAC) to undergo a similar reaction.

When polymerization takes place, the concentration of the monomer in the solution decreases while that of the polymer increases, which means that theoretically the percentage weight loss due to the monomer should decrease while that due to the polymer should increase. Experimental TGA runs were carried out on the monomer–polymer mixture of different known compositions and are shown in Figure 3. The weight loss due to the monomer step M1 decreases with the increase in the polymer concentration, whereas weight loss due to the polymer steps (P1 and P2) increases with the increase in polymer concentration. The decomposition steps M1 and P2 remains essentially unchanged in the ternary mixture. The monomer decomposition step M1 remains constant in the range 175°C (onset) to 247°C (endset), and the polymer step P2 also remain constant in the range 435°C (onset) and 467°C (endset). However, a clear shift in the polymer step P1 was observed. At relatively lower concentration of the polymer, the P1 decomposition occurs closer to the M1 step. As the concentration of the polymer increases, the P1 step shifts toward the P2 step. Also, the P1 decomposition occurs over a much broader range as the polymer concentration in the mixture increases. All this indicates that some interaction occurs between the monomer and the polymer under the condition of the experiment. However, it is difficult to ascertain the nature of interaction from TGA alone. The possible reasons for the interaction are under investigation.

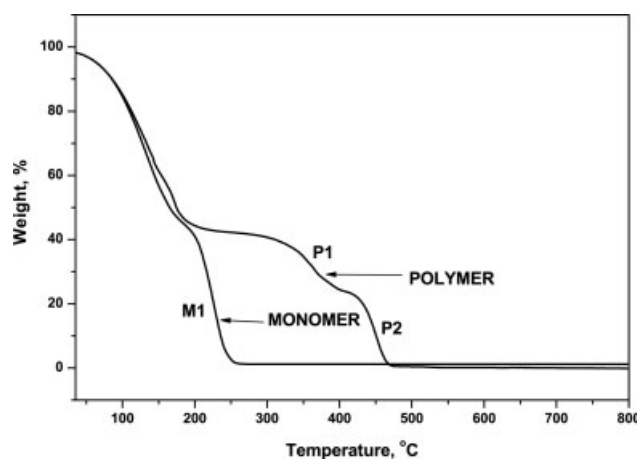


Figure 2 TG curve of DADM MAC and poly(DADM MAC) solutions in nitrogen atmosphere at a heating rate of $10^{\circ}\text{C min}^{-1}$.

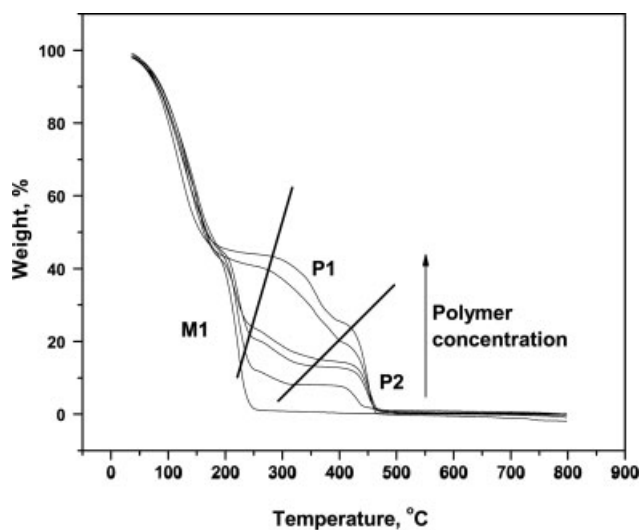


Figure 3 Experimental TG curves of DADMAC-poly(DADMAC) mixtures of various compositions.

From the TG curves shown in Figure 3, a calibration curve for the percentage weight loss of the monomer, Step M1, as a function of poly(DADMAC) weight fraction in the mixture was plotted and is shown in Figure 4. The poly(DADMAC) weight percentage is given as follows: $\text{poly(DADMAC)} / [\text{poly(DADMAC)} + \text{DADMAC}] \times 100$. A good colinearity was exhibited between the two parameters. The linear correlation factor (R) was found to be 0.9962. Similar calibration plot for the polymer decomposition step, P2, shown in Figure 5, yielded a very good R value of 0.9993. The polymer step P1 was not considered for generating a calibration plot because the weight loss in the step P1 is only 33% of the total weight loss of the polymer. Moreover, P1 depends strongly on the composition of the solution and shifts to higher temperature with the increase in polymer content.

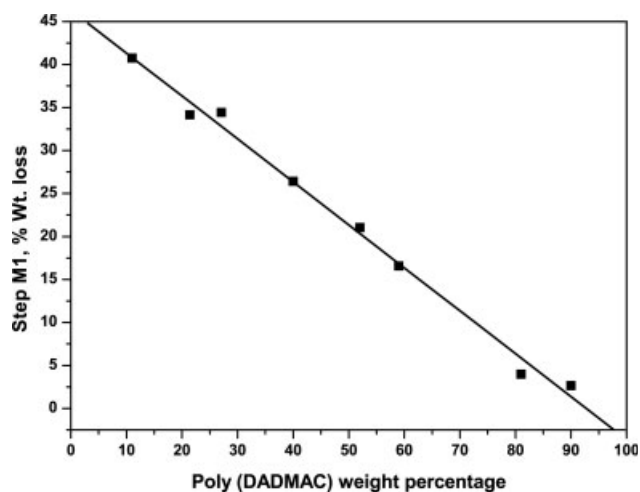


Figure 4 Percentage weight loss of DADMAC step M1 versus poly(DADMAC) weight percentage in the mixture.

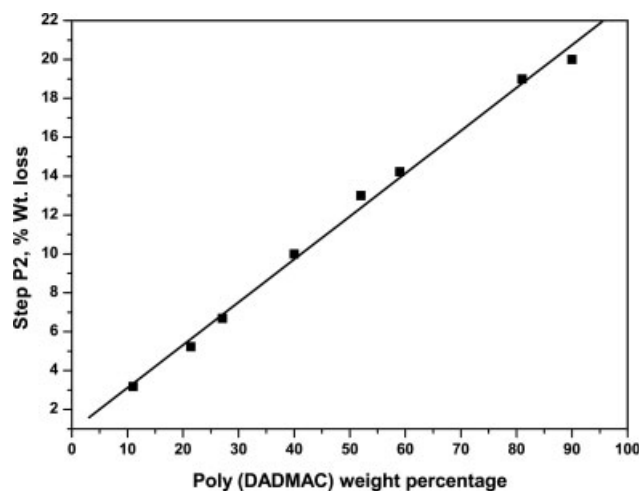


Figure 5 Percentage weight loss of the poly(DADMAC) step P2 versus poly(DADMAC) weight percentage in the mixture.

The DADMAC solutions were irradiated from 4 to 70 kGy without the use of any extraneous initiators or crosslinking agents. Since no crosslinking agents were used, gel formation does not take place, and the polymer formed up to the irradiated dose of 70 kGy is entirely soluble in water. After irradiation, the solution contains both the monomer and polymer in different ratios depending on the degree of conversion. Figure 6 shows the TGA curves of the irradiated samples. The thermal profiles of the samples are similar to that shown in Figure 3. As expected, the weight loss due to the monomer decreases and the weight loss associated with the polymer steps (P1 and P2) increases with increase in irradiation dose. As mentioned earlier, a shift in the polymer step P1 was observed, which depends on the concentration of the polymer in the mixture.

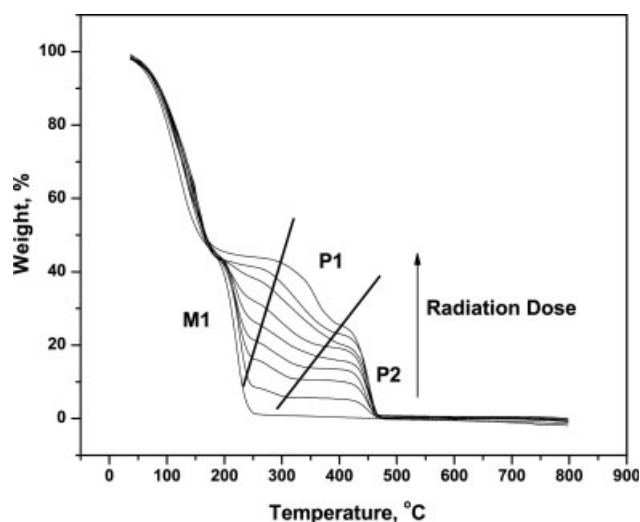


Figure 6 Experimental TG curves of the monomer exposed to various radiation doses.

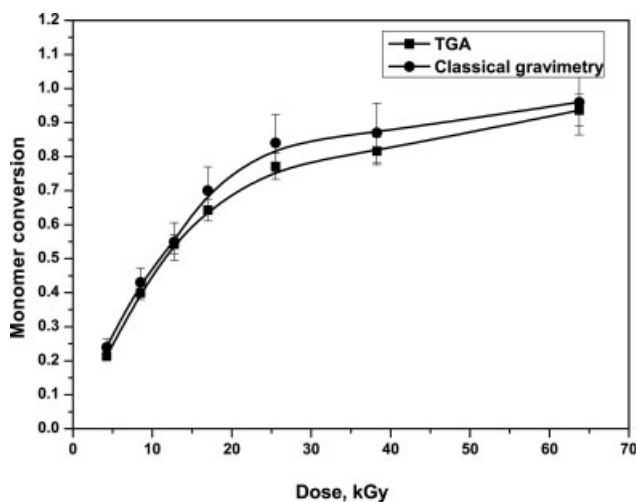


Figure 7 Degree of conversion of DADMAC as a function of radiation dose, calculated from classical gravimetry and TGA.

The P1 decomposition occurs closer to the M1 step at relatively lower concentration of the polymer and shifts toward the P2 step as the concentration of the polymer increases in the mixture. Also, a broadening of the P1 step was observed as the polymer concentration in the mixture increases. The weight loss of the monomer step M1 and polymer step P2 were noted, and the monomer conversion was calculated from the calibration plot generated previously (Figs. 4 and 5). Figure 7 shows the degree of conversion of the DADMAC to poly(DADMAC) as determined by TGA and classical gravimetry. Classical gravimetry studies were carried out to verify the results obtained from TGA studies. The monomer conversion values calculated from classical gravimetry was found to correlate with the TGA results within the statistical variation. The TGA measurements had an experimental variation of $\pm 5\%$, whereas the variation in gravimetric measurements was in the range $\pm 10\%$. Both classical gravimetry and TGA results indicates that the degree of conversion of the DADMAC increases steadily with the increase in the radiation dose up to a dose of about 40 kGy, after which it levels off.

CONCLUSIONS

A method of TGA is discussed to determine the concentration of the monomer DADMAC and poly(DADMAC) in DADMAC–poly(DADMAC) mixture without separation. The degree of conversion of the monomer determined using TGA were found to be in good agreement with that obtained using classical gravimetry. The degree of conversion of DADMAC reaches a value of 0.8–0.9 at a dose of 40 kGy, after which the increase in conversion is not very significant. TGA is a convenient and useful method to determine the degree of conversion of DADMAC to poly(DADMAC) as compared with hitherto established methods like ^1H NMR. It could be possible to extend this method to determine the degree of conversion of other monomers if the decomposition temperature of the corresponding polymer is well separated.

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