

## A New Method to Measure the Conversion of Radiation Polymerization of Electrolyte Monomer Diallyldimethylammonium Chloride in Dilute Aqueous Solution

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**Abstract:** The dependence of electrical conductivity on concentrations of diallyldimethylammonium chloride (DADMAC) monomer, linear poly(DADMAC) and their mixture monomer/poly(DADMAC) in dilute aqueous solution exhibits a linear relationship. It was possible to calculate conversion of DADMAC polymerization by measuring its electric conductivity. Although the electrical conductivity of the poly(DADMAC) solution decreased with increasing its molecular weight, in the process of UV or ionizing radiation polymerization the molecular weight of the polymers could be kept constant in the case of fixed temperature, UV-luminous intensity or dose rate. Based on the method mentioned above, the kinetics of UV induced polymerization of DADMAC in aqueous solution was studied; the overall activation energy of polymerization of DADMAC in the water phase was calculated to be  $18.8 \text{ kJ mol}^{-1}$ .  $\gamma$ -Radiation-induced polymerization of DADMAC in aqueous solution as a function of absorbed dose was studied as well. The conversion of DADMAC increased quickly with dose before 30 kGy and then increased slowly. The experimental data of both UV- and  $\gamma$ -induced polymerization were verified to be reliable by inverted ultracentrifugation method.

**Keywords:** poly(DADMAC), UV- and  $\gamma$ -induced polymerization, electric conductivity, conversion, reaction active energy.

### Introduction

Poly(DADMAC) with water soluble pyrrolidinium structure and permanent charge was synthesized via radical cyclopolymerization of DADMAC in aqueous solution. The structure of DADMAC, poly(DADMAC) and polymerization process were shown in Figure 1.<sup>2</sup> Due to versatile applications of poly(DADMAC), such as in food, medicine and wastewater treatment industry, many research works involving the polymerization mechanism, kinetics, structure as well as properties of polymer have been studied in detail since eighties of last century,<sup>3-5</sup> while the information on UV- and  $\gamma$ -radiation polymerization of DADMAC in aqueous solution has received less attention than the great number of commercial applications of this polyelectrolyte. Generally, chemical methods or isolation and weighing of polymer are used to measure the rate of polymerization. The dilatometry is also a common method to be used. These methods are not fit to deal with polyelectrolytes in solution because of long time consuming and low accuracy. In dilatometry, the decrease in volume on polymerization is hard to be observed in UV- or

$\gamma$ -radiation field. It is well known that DADMAC and poly(DADMAC) can be regarded as strong cationic electrolytes in dilute aqueous solutions.<sup>1</sup> The equivalent conductivity ( $\Lambda^\circ$ ) of DADMAC in infinite dilution equals to  $111.1 \text{ s} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$  and there is a linear correlation between the specific conductivity and its concentration.

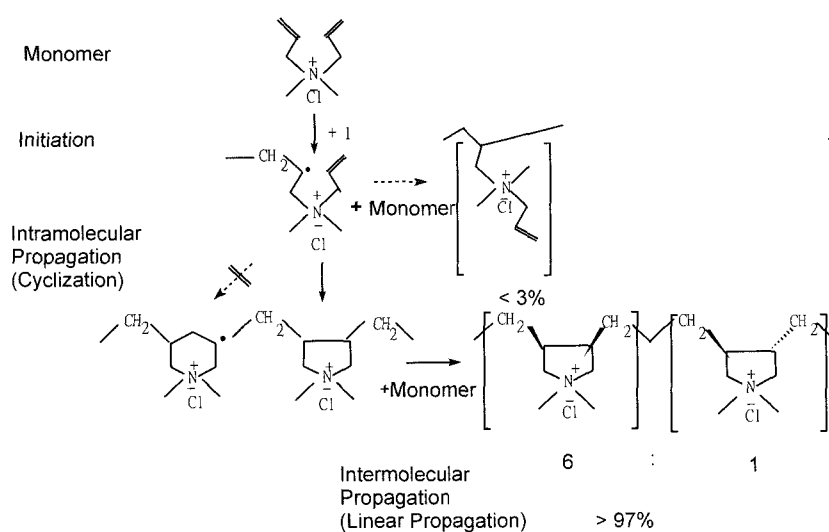
The work showed that the specific conductivity of poly(DADMAC) and DADMAC/poly(DADMAC) mixture low content polymer with monomer DADMAC also has linear dependence on the concentration, respectively. Based on these facts, the electrical conductivity analysis can be used to measure the concentration of polyelectrolytes in dilute aqueous solution. The advantages of this method lie in its simplicity, expeditiousness, and precision because no need to separate monomer and polymer. In this work the results for the kinetics and overall activation energy of UV induced polymerization as well as the conversion of radiation polymerization of DADMAC will be reported.

### Experimental

**Instruments and Reagents.** The Digital Electric Conductivity Detector (model DDS-307, Shanghai, China), UV Chemical Reactor (light density  $7 \times 10^3 \mu\text{w} \cdot \text{cm}^{-2}$ , self-made,

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**Figure 1.** Schematic layout of DADMAC and poly(DADMAC) structure and process of polymerization.

Metal Factory in Department of Technical Physics, Peking University), and Ultrafilter centrifuge apparatus (SM13229E cut off 5000, SM 13249E cut off 20000, Germany) are used. DADMAC (60% aqueous solution, TCI Tokyo Kasei Kogyo Co.Ltd., Japan) was used as received.

**Preparation of Poly(DADMAC).** 60% of DADMAC solution was poured into a quartz glass tube that was sealed after bubbling with  $N_2$  for 20 min, followed by irradiation in UV reactor for 4 hrs. The resulting sample was dissolved in deionized water and precipitated with acetone for 2~3 times, white floccule was dried and grinded into powder, finally put into 50°C vacuum chamber until the weight of the sample was constant. The weight average molecular weight of the poly(DADMAC) ( $M_w = 3.57 \times 10^5 \text{ g} \cdot \text{mol}^{-1}$ ) was measured by using low-angle, laser light scattering instrument (model DLS-700, Japan). The density of polymer ( $\rho_{25^\circ\text{C}}$ ) was  $1.20 \text{ g} \cdot \text{cm}^{-3}$  measured by pycnometry. Crystallinity of polymer is 14.2% analyzed by x-ray diffraction method (model RM-102, Japan).

**Calibration Curve.** In order to reduce the experimental error, unirradiated samples should be used as a control in making the calibration curve, the abscissa is the batching conversion of DADMAC, that is, under the conditions with the conversion lower than 10%, to prepare various content of poly(DADMAC) in monomer- polymer mixed solution as the calculated conversion; the ordinate is the difference of electrical conductivity ( $\Delta\kappa$ ) induced by the change in conductivity from a certain weight of monomer to that of respective polymer. In this condition, electrical conductivity of samples before and after irradiation (unirradiated samples as the control solution) was measured and could be calculated. So the conversion of monomer would be obtained from the calibration curve.

**Measurement of Conversion of DADMAC by Conduc-**

**tivity Method.** 4.00 mL 60% DADMAC was poured into quartz glass tube (glass tube was used in  $\gamma$ -radiation), which was sealed after removing oxygen by bubbling with  $N_2$  for 20 min. The tubes were irradiated for different time in UV reactor or Co-60 source. The irradiated samples were diluted by deionized water to a suitable volume and electric conductivities were measured at  $25 \pm 0.1^\circ\text{C}$ . And the conversion was calculated by the method mentioned above.

**Measurement of Kinetic Constant.** The above process were repeated at various temperature ( $14\sim 50^\circ\text{C}$ ), reaction rates of UV induced DADMAC polymerization in different temperature were calculated. Therefore, the overall activation energy could be deduced with Arrhenius empirical equation.

**Measurement of Conversion by Inverted Ultra-Centrifugation Method.** In order to verify the method, the sample was put into the external part of ultrafilter centrifugal tube, which was kept in 3500 r/min centrifuge separator until the weight of the external tube getting to constant. The samples in internal and external tubes were transferred into weighed bottles separately, washed for several times and then the bottles were dried at  $100^\circ\text{C}$  to constant. The samples in internal and external tubes were weighed ( $W_{ex}$  and  $W_{in}$ ) separately and the conversion was calculated by the following equation:

$$\text{conversion \%} = W_{ex} / (W_{ex} + W_{in}) \times 100 \quad (1)$$

## Result and Discussion

**The Relationship between Conductivity and the Concentration of DADMAC, Poly(DADMAC) and Their Mixture.** Wandrey's investigation revealed that dependence of the conductivity on the concentration of DADMAC could be expressed in eq. (2)<sup>2</sup>:

$$\kappa_m = \kappa_0 + \Lambda_m^0 C_m + C_m \Phi(C_m) \quad (2)$$

$\kappa_m, \kappa_0$ : electric conductivity ( $\mu\text{S} \cdot \text{cm}^{-1}$ ) of DADMAC and solvent (solvent here is water) respectively

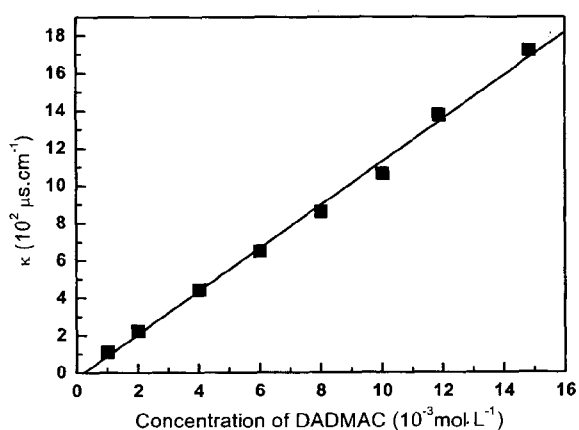
$\Lambda_m^0$ : equivalent conductivity at infinite dilution

$C_m$ : DADMAC concentration ( $\text{mol} \cdot \text{L}^{-1}$ )

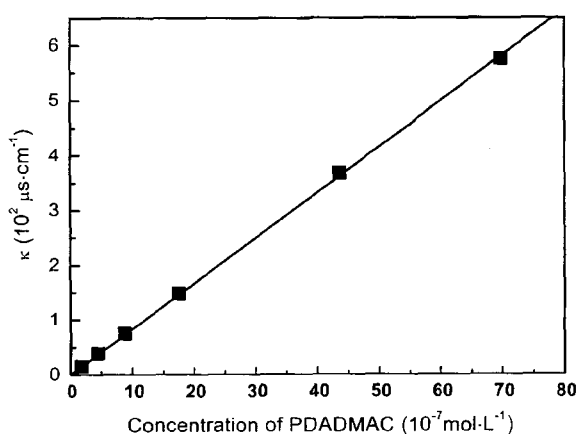
$\Phi(C_m)$ : effect of interionic interaction on conductivity

DADMAC concentration in the experiment is less than  $10^{-2} \text{ mol} \cdot \text{L}^{-1}$ , and water conductivity is as low as  $1.68 \mu\text{S} \cdot \text{cm}^{-1}$ , the two terms of  $C_m \Phi(C_m)$  and  $\kappa_0$  could be neglected, so  $\kappa_m$  has linear dependence only upon  $C_m$ . The conductivities measured at various DADMAC concentration ( $0 \sim 1.6 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ ) were illustrated in Figure 2. It exhibited a high co-linearity between two parameters (linear correlation factor  $R = 0.9995$ ). In addition, equivalent conductivity calculated from the graph is  $108.7 \mu\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ , close to the literature value,  $111.1 \mu\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ .

Poly(DADMAC) is also a strong electrolyte, the relation



**Figure 2.** The conductivity as a function of DADMAC concentration.



**Figure 3.** The solution conductivity as a function of poly(DADMAC) concentration.

between its concentration and conductivity in dilute solution could be expressed in approximate way as eq. (2)<sup>2</sup>:

$$\kappa_p = \kappa_0 + \Lambda_p^0 C_p + C_p \Phi(C_p) \quad (3)$$

In dilute solution ( $0 \sim 7.0 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ ), basing on the same reason as mentioned above, a nice linear correlation between  $\kappa_p$  and  $C_p$  was obtained as well (Figure 3, the linear correlation factor  $R = 0.9998$ ). The conductivity of DADMAC and poly(DADMAC) as mixed solutes in dilute solution has additivity. Eq. (4) shows overall conductivity of mixed DADMAC/poly(DADMAC) solution.

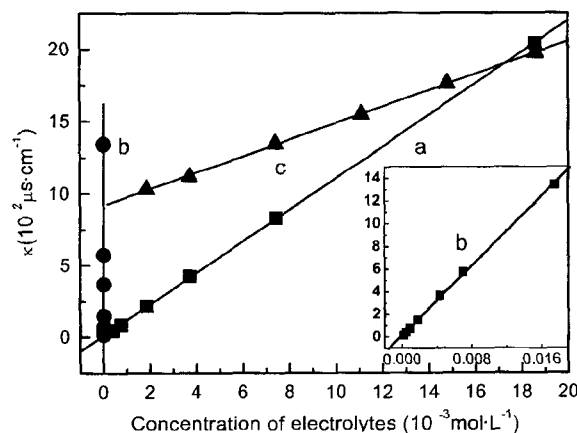
$$\kappa_{mix} = \kappa_0 + \Lambda_m^0 C_m + \Lambda_p^0 C_p + C_p \Phi(C_m, C_p) + C_p \Phi(C_m, C_p) \quad (4)$$

Fixing the total concentration of DADMAC and poly DADMAC ( $C_0$ ), and  $C_p = C_0 - C_m$ , the correlation function could be derived  $\kappa_{mix} = f(C_m)$ , the overall conductivity could be functioned by DADMAC concentration (see Figure 4). Curve *c* in Figure 4 shows that the overall conductivity of the mixed system has linear dependence on DADMAC concentration. When the DADMAC content in mixed solution is high, the conductivity was mainly contributed by DADMAC, if the content of poly(DADMAC) gets higher to a certain degree, the contribution of poly(DADMAC) to conductivity should not be ignored.

**Kinetics Study of UV Induced Polymerization of DADMAC at Low Conversion.** The reaction rate  $v_p$  in radical polymerization (both UV- or  $\gamma$ -induced polymerization of vinyl monomer are free radical process) can be functioned of initial monomer concentration ( $C_0$ ) and monomer conversion  $C$ :

$$v_p = C_0 \frac{dC}{dt} \quad (5)$$

The conversion at different time may be calculated from curve *c* in Figure 4. Depending on the co-linearity of con-



**Figure 4.** The dependence of conductivity on the concentration of DADMAC (a) poly(DADMAC) (b) or DADMAC/poly(DADMAC) (c).

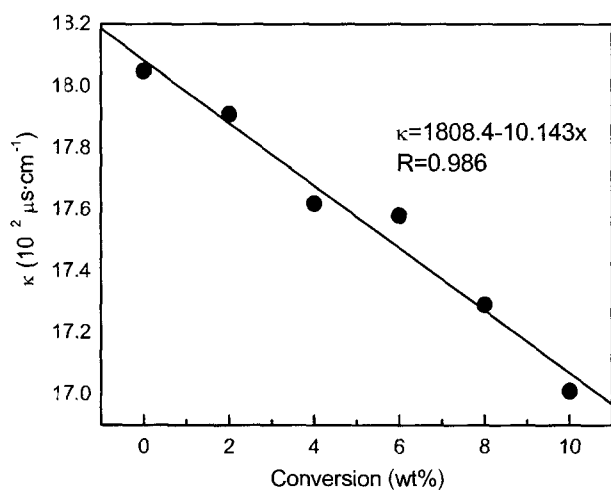
version and corresponding time  $t$  in low conversion ( $< 6\%$ ),  $dC/dt$ , the slope of the straight line, was obtained. From eq. (5),  $v_p$  could be determined. However, it is easy to cause error in this way because comparing with relative higher electric conductivity of the sample (about  $1800 \mu\text{s} \cdot \text{cm}^{-1}$ ), the conductivity changes of samples at low conversion are rather low (less than  $100 \mu\text{s} \cdot \text{cm}^{-1}$ ). It means that the error in sampling, stability of instruments or accidental error may be high enough to mask the conductivity change caused by monomer conversion. In fact, this kind of error can be deducted by calculating conversion not directly from corresponding solution conductivity, but from difference of conductivity ( $\Delta\kappa$ ) after and before irradiation, the later one is as the control solution just like in colorimetry. The physical meaning of  $\Delta\kappa$  is the decreased value in conductivity caused by transferring certain amount: monomer electrolyte to polyelectrolyte. The calibration curve was obtained (Figure 5, 6) according to the method mentioned in experimental section. The kinetics curve of the conversion could be plotted with the data of conversion calculated from Figure 6 and corresponding reaction time at different temperature (Figure 7). Figure 7 exhibited relative high linear dependence of kinetic curves ( $14\sim 50^\circ\text{C}$ ,  $R$ , linear correlation, greater than 0.98). With the aid of eq. (5) and Figure 7, polymerization rate ( $v_p$ ) at different temperature were calculated.

According to Arrhenius empirical equation, reaction rate constant  $\kappa$  dependence on activation energy  $E_a$  was shown in eq. (6):

$$\kappa = A \exp(-E_a/RT) \quad (6)$$

Logarithmic form of eq. (6) can be written as:

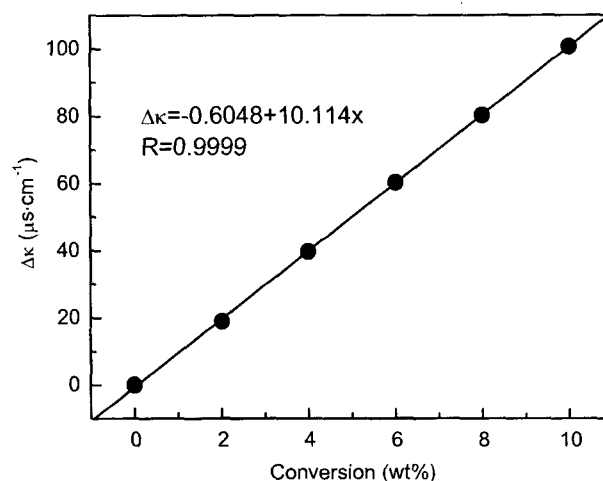
$$\ln \kappa = \ln A - E_a/RT \quad (7)$$



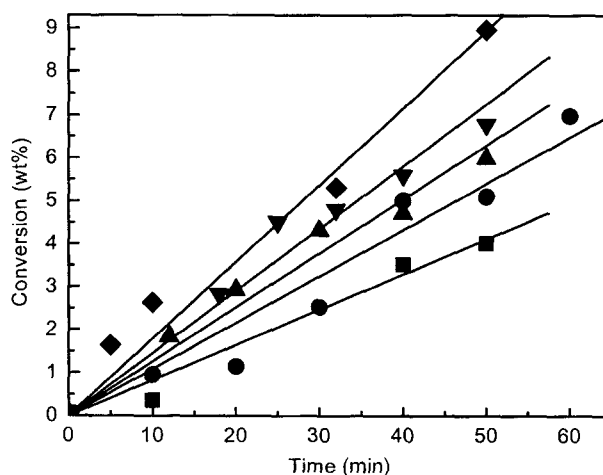
**Figure 5.** The change of electric conductivity with DADMAC conversion.

Reaction rate  $v_p$  was used instead of  $\kappa$  in this work at low conversion,  $\kappa$  could be regarded linear dependence on  $v_p$ . Plot  $\ln v_p$  with  $1/T$  (Figure 8), the overall activation energy  $E_a$  can be deduced to be  $18.8 \text{ kJ} \cdot \text{mol}^{-1}$  from the slope of the line.

Electrical conductivity analysis method to measure the conversion is not reported yet. In order to verify the method, inverted ultracentrifugation method was used. In fact, this process is gravimetric analysis of conversion. Process of separating unreacted monomer and polymer was achieved not by precipitation but by high-speed centrifuge effect in aid of different porosity of ultracentrifugation tube. Standard mixed solution sample of 8% polymer content was measured by inverted ultra-centrifugation as well as conductivity respectively yielding results of 8.4 and 7.7%. Similar data



**Figure 6.** Calibration curve of the conversion of DADMAC polymerization induced by UV-irradiation.



**Figure 7.** Kinetics curves of DADMAC polymerization induced by UV-irradiation. (■)  $14.0^\circ\text{C}$  (Slope,  $8.70\text{E-}4$ ); (●)  $21.6^\circ\text{C}$  ( $1.08\text{E-}3$ ); (▲)  $28.5^\circ\text{C}$  ( $1.27\text{E-}3$ ); (▼)  $35.4^\circ\text{C}$  ( $1.47\text{E-}3$ ); (◆)  $42.6^\circ\text{C}$  ( $1.70\text{E-}3$ ).

were obtained at 4% polymer content in standard sample. Standard samples conversion measured by the conductivity was a bit low compared with that gained by the ultracentrifugation method; relative error is less than 5%. Comparison of the two methods showed that the recommended method here is reliable and feasible.

**Study on  $\gamma$ -Radiation Polymerization of DADMAC in Aqueous Solution.** Free radical polymerization of DADMAC in aqueous solution can be initiated by radiation in vacuum. The experimental results revealed that without crosslinker, the polymer produced by  $\gamma$ -irradiation polymerization is entire linear before 30 kGy, which can be dissolved in water slowly. Samples were irradiated for different time under a certain dose rate ( $41.1 \text{ Gy} \cdot \text{min}^{-1}$ ) at room temperature and the conductivities of the irradiated samples were measured

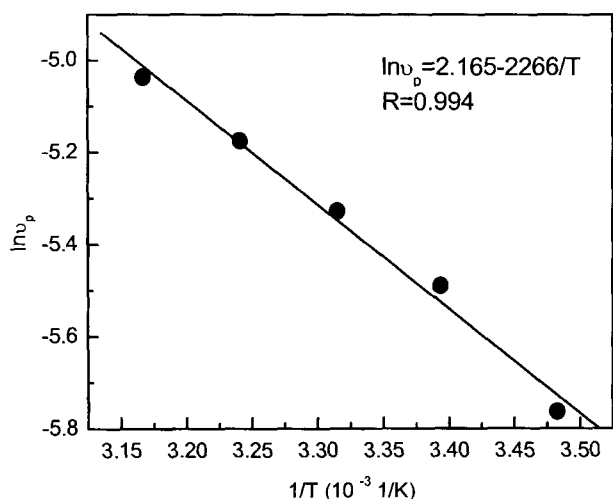


Figure 8.  $v_p \sim 1/T$ .

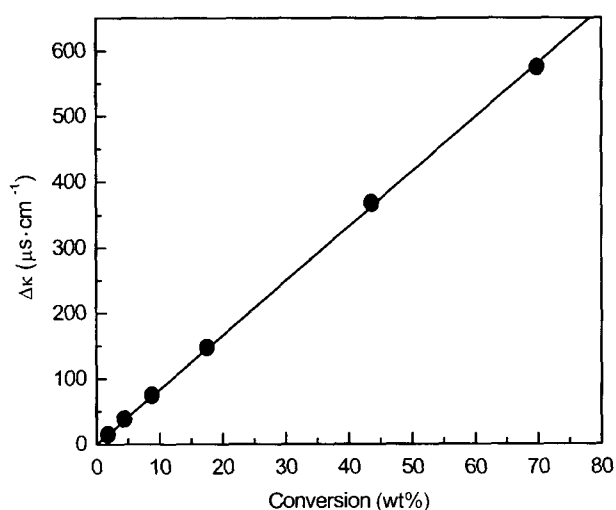


Figure 9. Calibration curve of the conversion of DADMAC polymerization induced by  $\gamma$ -irradiation.

separately. Conversions were calculated with the calibration curve shown in Figure 9 (plotted in the same way as Figure 6 only range of conversion up to 80%). Therefore, the graph of conversion versus dose can be plotted. Figure 10 illustrated that the conversion of DADMAC increased significantly with increase of dose before 30 kGy and then this increase tendency became slow at higher dose. The result was also verified by inverted ultracentrifugation method, relative error is also about 5%. It should take notice that electric conductivity of linear poly(DADMAC) in dilute solution decreases slightly with increase of average molecular weight. Fortunately, the average molecular weight of poly(DADMAC) formed from radiation (UV and  $\gamma$ -ray) polymerization under certain intensity (in UV) or dose rate (in ionizing radiation) and same temperature could be kept constant.

## Conclusions

A new method of electrical conductivity analysis is introduced to determine solute content in organic electrolyte monomer DADMAC, polyelectrolyte poly(DADMAC) as well their mixture in dilute aqueous solution. Concentration of polymer in mixed DADMAC-poly(DADMAC) solution could be directly measured without separation. As the applications, Kinetics of UV induced DADMAC polymerization in dilute solution was studied, the activation energy  $E_a$  of UV polymerization reaction equals to  $18.8 \text{ kJ} \cdot \text{mol}^{-1}$ .  $\gamma$ -radiation induced DADMAC polymerization in dilute aqueous solution was also investigated with this method. The results revealed that monomer conversion increased significantly with dose before 30 kGy. In order to get high repeatability, one should be very careful in the experiment. Repeated measurement shows relative standard deviation of this method to be less than 1%, and relative error is less than 5%

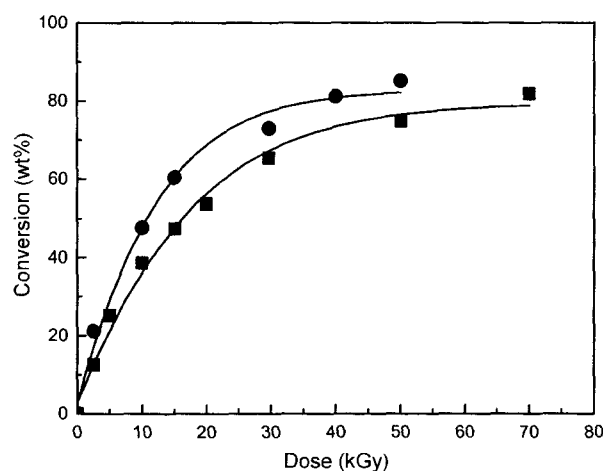


Figure 10. The conversion of DADMAC polymerization induced by  $\gamma$ -irradiation as a function of dose [DADMAC] = 50%. Dose rate =  $41.1 \text{ Gy} \cdot \text{min}^{-1}$ . (■) conductivity analysis and (●) inverted ultracentrifugation method.

comparing with inverted ultracentrifugation method. Simple instrument and process as well as rapidity would make this method valuable in radiation polymerization of electrolyte monomer.

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