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*Article*

# A Study On The Use Of DSC And TGA Techniques For The Characterisation And Synthesis Of Surface Water For A Monomeric Colloidal Polymer

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**Abstract:** This study examined and evaluated the properties of surface water using differential scanning calorimetry (DSC), through which several factors were measured, in particular the charge density in water layer, which has a thickness ranging from approximately 0.45 to 0.75 nanometres, The surface water was characterised by a higher density than that of mineral water, and its density is high depending on the surface density , The evaporation of the polymer solution produced in the study was also measured using thermogravimetric analysis. The results showed that it is distorted by forces known as electrostatic repulsion, which occur between air and water, It was found that the polymer increases the evaporation rate of mineral water, whilst surface water evaporates more slowly compared to free water. Ultimately, it can be said that the synthesised polymer has promising applications, as it can be incorporated into water-based coatings to stabilise them through freezing and thawing and to extend their shelf life, and it also has promising pharmaceutical applications.

**Keywords**: DSC, density charge , mineral water , surface water , tetrahydrofuran.

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## 1. Introduction

Over the past 20 years, there has been significant advancement in polymer nanoparticles based on single polymer chains. Particle sizes range from 1 to 20 nm [1-4]. and the production is mostly reliant on the folding or collapse of individual polymer chains Because of their tiny size and vast range of chemical compositions[5], these nanoparticles are anticipated to have special qualities and functionsMany studies have focused on regulating the structure Single-chain polymers. And the surface water to which these particles are bound in the aquatic environment, however, has received little attention.This dissertation will concentrate on the impact of nanoparticles on aquatic systems and surface water. The Van De Mark group created the Colloidal Unimolecular Polymer particle, or CUP, which is the particular kind of single chain nanoparticle in question.The creation of single chain nanoparticles can be done in a variety of ways. Here are some instances of the strategies being used. Furthermore, there are several instances of globular particulate proteins. Both graphene and fullerene-type structures are single-molecule particles.

None of the systems are inexpensive to prepare, nor can their size and surface ion content be readily changed. CUP are inexpensive and easily customizable. A novel kind of spherical particle known as colloidal unipolymer (CUP) is formed when a single polymer chain breaks down. Depending on the molecular weight, it can exist as solid spherical particles in aqueous mediums with diameters ranging from 4 to 10 nanometers. These nanoparticles, which have a hydrophobic core and hydrophilic groups on their surface, are sustained in water via ionic repulsive interactions.Because of hydrogen bonds, a layer of water is trapped or bonded to the surface of CUP. Any kind of monomer may be used to create CUP polymers using any polymerization techniqueIt It should be mentioned that the HLB value—the proportion of hydrophilic to hydrophobic monomers in the polymer chain—is very important.

Elevated The polymer may become liquid or fail to form a spherical shape if it is very hydrophilic; it tends to agglomerate if it is overly hydrophobic [6–11]. Van De Mark et al. have so far successfully created CUP systems from amine cross-linkers, quaternary salts [13] , and so forth. CUP particles were produced by a procedure called "hydration" following the polymer's purification Figure (1). A water-miscible solvent having a low boiling point, was used to dissolve the polymers. To guaranty that every polymer chain was in a random coil shape, Structure I, stirring was done overnight. In order to create salts, a base was gradually added to the mixture until the pH reached 8.5. Because of charge repulsion, structure II, the chains grew longer. The ions dissolved and separated when the pH was changed and water was progressively added. Structure III: At a critical ratio between water and the solvent, the Mark-Hewitt coefficient reaches its maximum value, the interaction between the polymers becomes greater than the interaction between the polymer and the solvent, and the hydrophilic groups (salt) orient themselves toward the aqueous phase. The increased electrical insulation caused by the added water increased the repulsion between neighboring ions and the chains toward a linear shape, resulting in increased viscosity [4]. arranging themselves to provide the greatest amount of charge separation. As a result, the hydrophobic polymer chain collapses to take on a spherical form, Structure IV, and the polymer's backbone releases more water, which raises entropy. Finally, the low-boiling-point solvent is extracted at a reduced pressure. The ionic groups on the surface act as a driving force by electrostatic repulsion, preventing the particles from grouping together. These particles, once formed, constitute a thermally stable water solution [14–20].

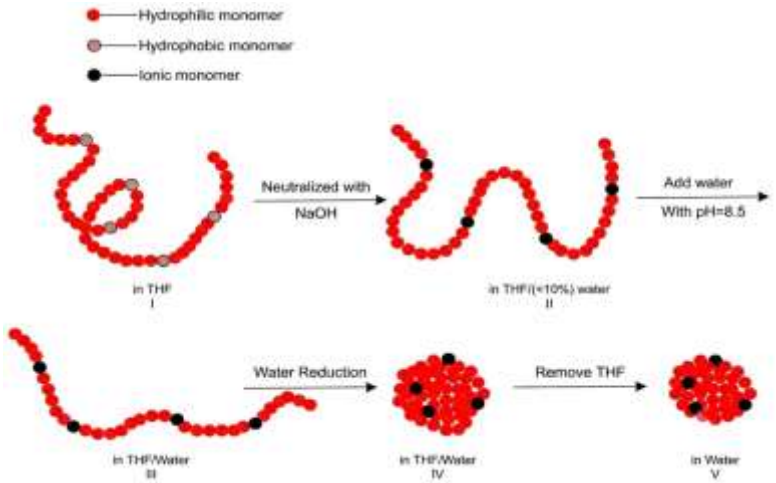


FIG.1. A diagram illustrating the reduction in water consumption and the establishment of a polymer’s unit

## 2. Materials &Method

We purchased methyl methacrylate, methacrylic acid, 2-methylpropiontrile and 1-dodecanol. To purify methyl methacrylate, it was washed in a 15% sodium bicarbonate solution, rinsed with deionized water and saline solution, dried with sodium sulfate, and filtered. Copper bromide was utilized as an inhibitor, which was then distilled using nitrogen gas. Methacrylic acid was recrystallized from methanol after low-pressure refining with copper bromide, drying, and distillation under nitrogen protection. which were synthesised by THF (tetrahydrofuran) polymerisationAfter adjusting the molecular weight of the synthesised polymer, we added ten moles to a three-necked flask with a capacity of two litres. We then added methyl methacrylate and methacrylic acid, each in

a specific proportion that differed from the other, and 1-dodecanol was added as a chain transfer agent, along with two moles of monomer, or 0.00085 of the AIBN catalyst, were then added. Positive nitrogen pressure was maintained throughout the polymerization process thanks to the employment of a condenser and gas outlet coupled to an oil filter, as well as the reaction's nitrogen-rich environment. Once the process was complete, the temperature of the mixture was raised to boiling point; during this time, stirring continued from the start until 24 hours had elapsed. We then cooled the polymer solution to room temperature and removed the tetrahydrofuran using a rotary evaporator. Finally, we precipitated the polymer in cold, ion-free water, after which we dried it in a vacuum oven at 300 Kelvin for a further 24 hours.

To reduce the water content, 500 ml was added along with 15 g of dry polymer and 50 g of tetrahydrofuran to a beaker, and we stirred the mixture for 24 hours until the polymer chains had formed coils. A 2 molar ammonia solution was then slowly added to adjust the solution's pH to 8.5. We then prepared a CPU solution, consisting of an organic compound, by adding 100 g of deionised water with a pH of 8.5 to the beaker at a flow rate of 1.24 g/min, whilst maintaining a constant pH. We then evaporated the tetrahydrofuran under vacuum and filtered it through a 0.45-micrometre filter.

As for the characterisation of the polymers, the molecular weight was determined using a GPC analyser with a TDA 305 detector and a PAM-505 column at a flow rate of 0.75 ml/min of tetrahydrofuran and a 125-microlitre injection volume for samples with a concentration of 2.5 mg/cm³. The density of the solutions was measured using a DDM 2911+ at 300 K, and the dried polymer was measured at 330 K and 390 K using an AccuPyc 1340 at 310 K. Viscosity measurements were carried out using the Ubbelohde-304 at 310 and 300 Kelvin. Particle size analysis of the diluted solutions (15% wt) was carried out using the DLS technique on a MicroTrac NanoTrac 250 by applying the Stokes modification. Finally, DSC thermal analysis was carried out using a TAQ 2000 on 30 nL samples in hermetically sealed vials at a heating rate of 5 K/min up to 320 K.

## 3. Results & Analysis

### 1- Analysis based on the cooling rate and ice formation

Figure (2) illustrates DSC measurements taken in tightly sealed Tzero jars containing about 35 mg of CUP solution. A sufficient headroom was supplied at the top of the tank to prevent explosions or leaks during the freeze-thaw cycle and to ensure reliable measurements. The DSC samples were chilled to 250 K and held there for 10 minutes to ensure that all freezeable water had frozen; they were then heated to 320 K to melt the ice while preventing leaks. Because there was considerable overcooling throughout the cooling sweep, it was challenging to pinpoint the precise location of the ice formation peak. Therefore, only the heating and melting processes are represented by the data shown here. Only experiments with losses of less than 0.0 0 25 mg were used; the mass of the DSC cell was measured both before and after the experiment to ensure that no water was lost during the cycle. For 20 minutes, samples of a 20% solution of 35 k CUP, Polymer 2, were heated to 250 K at a rate of 15 K/min while keeping the temperature steady. After that, they were heated to 320 K at a rate of 5 K/min to determine how long it would take for the sample to freeze and if surface water would eventually separate from the outer surface and freeze. The isothermal holding period was adjusted to two, three, six, and eight hours while the same sample was analyzed using the same methodology.

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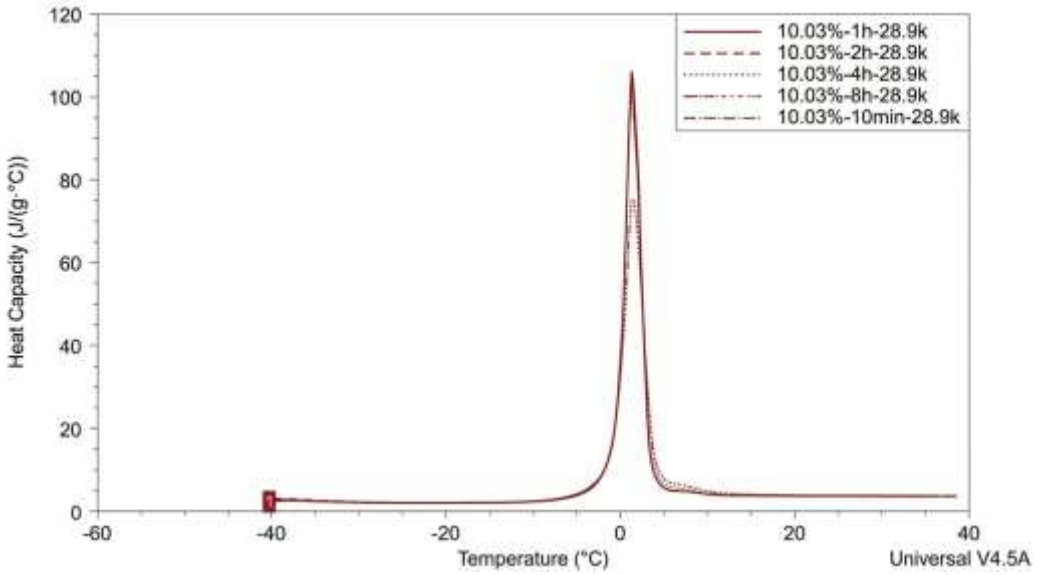


FIG.2. The melting point of a fixed proportion of the polymer at different times during thermal equilibrium.

**2- Surface water for each portion of the polymer blend at different weight ratiosand at different cooling rates.**

At a cooling rate of 10 K/min, solutions with a weight percentage of CUP of 21.40% or more demonstrated a decrease in the quantity of surface water per particle, Figure (3). The condensation of counterions between the molecules was the cause of this decrease. Counter-ion condensation between particles happens even before the cooling process starts when the weight % of CUP is large and there are short distances between CUP particles. Additionally, with slow freezing rates, the development of ice due to charge condensation was decreased by this counter-ion condensation between particles. The effect of slow freezing lessens as the concentration rises, and at around 36%, the surface water stabilizes and becomes independent of the chilling rate. It is noteworthy that the CUP solution's viscosity increases quickly when Manning condensation begins and is dependent on concentration. Ionic repulsion slows down the diffusion rate of CUP particles, making it harder for them to separate from the forming ice crystals; as a result, the CUP particles become inclusions.

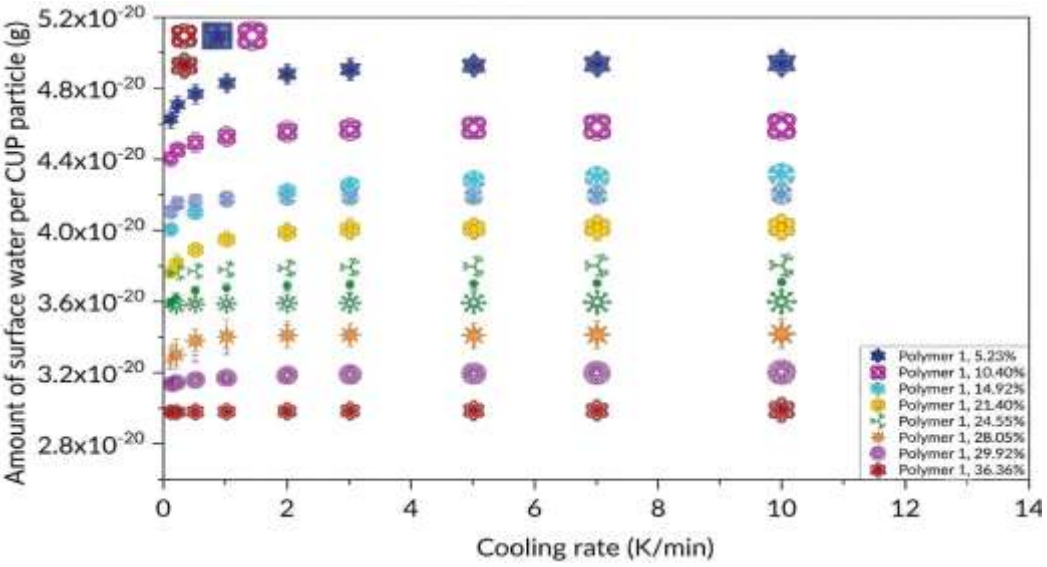


FIG.3. Different weight ratios at different cooling rates, with the volume of surface water per unit of polymer

**3- The surface tension of polymer molecules produced at different weight ratios, and at cooling rates ranging from 0.1 Kelvin per minute to 10 Kelvin per minute**

Figure (4) illustrates the difference between the components of surface water with different weight ratios in the synthetic polymer solution; as the solution's ratio to the synthetic polymer increases, the cooling effect disappears completely, with the partial adaptation index of the ions found to be below the initial concentration. It was found that the product of the partial ionisation reaction of counter-ions and the viscosity product contributed to regulating the system by approximately 20 per cent. The surface water reached a point where the cooling effect was no longer present, thereby approaching the coagulation and freezing point which restricted particle movement, whilst the cooling rate reached 0.1 K/ minute, compared with 10 K/minute, as shown in Figure 4. The surface water retained its properties, which is consistent with Manning's theory, whereby as concentrations increased, the variations decreased and reached zero at the point of coagulation.

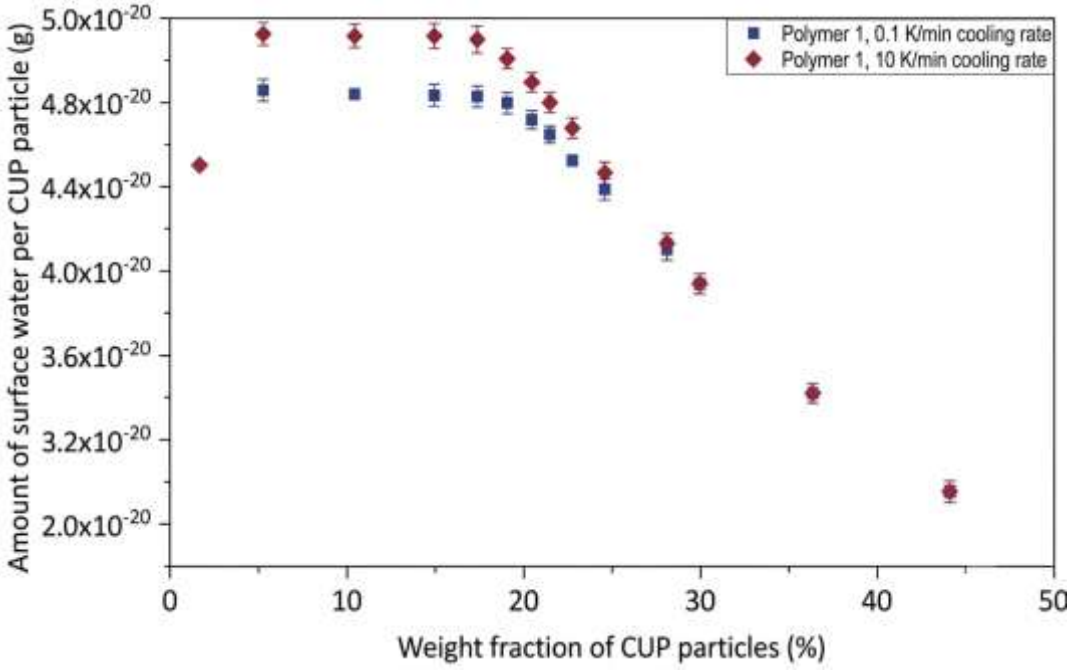


FIG.4. Variation in the composition of surface water with different weight ratios in the manufactured polymer solution

**4- The effect of melting temperatures on the resulting polymer blend at different weight ratios**

All CUPs were cooled at 10 K/min rate, which is the highest cooling rate that can be achieved by the DSC equipment, in order to reduce the effect of counter ion condensation as much as possible for the rest of this study. The CUP samples were heated up to 313.15 K at a rate of 3 K/min following the thermal equilibrium stage of 10 minutes. Moreover, heat of fusion of the water sample, which was mixed with NaOH, was measured during the neutralization of the CUP samples by NaOH. The values of heat of fusion and melting points of NaOH treated and deionized water were same (333.5 J/g) so deionized water was taken as reference. Different weight ratios of CUP solutions with different molecular weights of polymers were prepared. Heat of fusion of each CUP solution was calculated by using DSC analyzer. The graph shown in Figure 5 shows the peaks of heat absorption in DSC for Polymer 1 CUP solutions at different weight ratios. There was an obvious shift towards lower temperatures in the maxima of heat absorption as the weight ratio increased; this phenomenon could be attributed to the effect of Raoult's law of CUP in the given range. The number of particles generated as a

consequence. The high molecular weight of Polymers 1, 2, and 3 with a ratio of MAA : MMA 9:1 leads to a smaller slope since there is less surface area per gram of the polymer. Density of ionic charges on the CUP surface is also an important aspect to take into consideration. As all the ionic groups are often concentrated on the surface, increasing the molecular weight with a constant ratio of MMA:MAA leads to higher surface charge density.

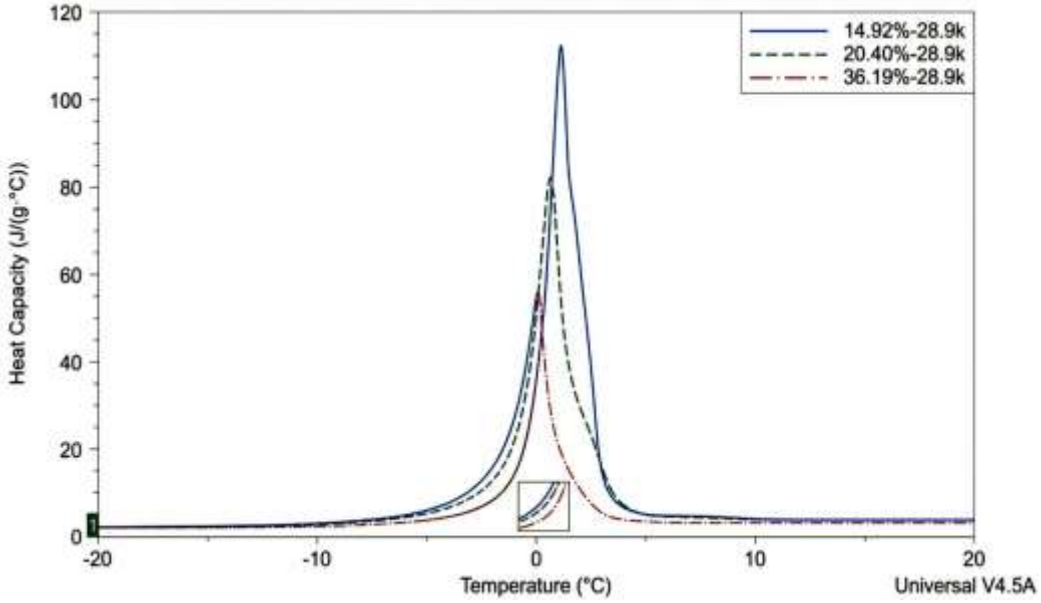


FIG.5.Heat absorption peak curves for three different weight fractions of the manufactured polymer

**5- The effect of the weight ratios of surface water on the different types of resulting polymers (CUPs) with varying monomer ratios as a function of the weight ratio of each type of CUP**

Weight percent of surface water and CUP is given by Figure 6. It can be seen from the data that there was a considerable amount of non-freezeable water in this system. In the given range, the weight percent of CUP exhibited a linear relation with water. This resulted in all the particles containing an equal amount of water. Molecules Polymers 1, 2, and 3 are characterized by higher molecular weight and a ratio of 9:1 for MMA to MAA, leading to a steeper slope, since the surface area is less per gram. The surface density of ions in the CUP surface is another variable that comes into play. All charged groups tend to be in the surface, and thus the higher the molecular weight with a ratio of 9:1, the higher the surface density of ions.

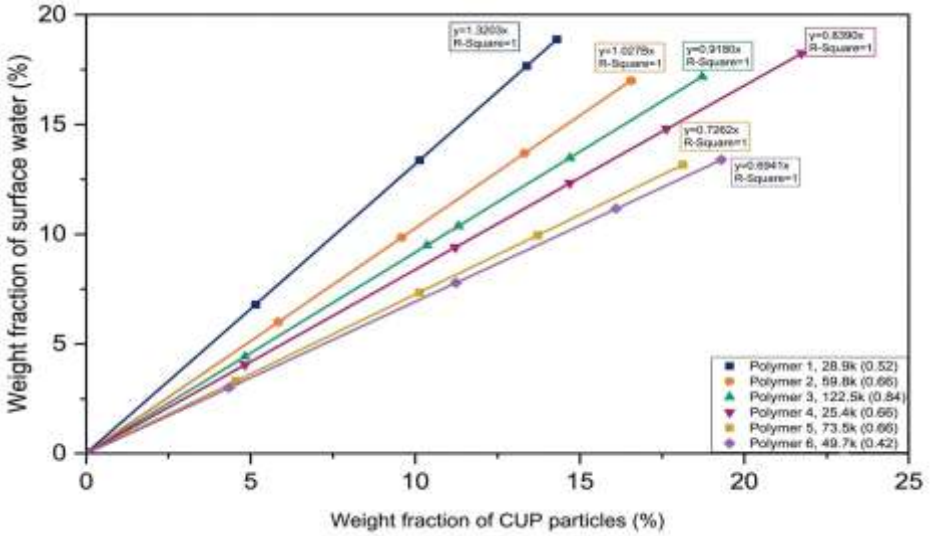


FIG.6. The weight percentage of surface water relative to the manufactured polymer

**6- The weight ratio of manufactured polymer molecules compared with the weight ratio of surface water compared with**

Figure (7) demonstrates that the weight percentage of water starts to stabilize at about 35% at concentrations over 20%. As the concentration rises, the distance between the ions decreases and the contact between counter-ions between molecules increases. This interaction lowers the effective surface charge and causes Manning condensation. The wetting layer diminishes as the charge does. By tracking the moment at which the curve turns non-linear, one may utilize the linear behavior at low concentrations to ascertain when Manning condensation becomes apparent.

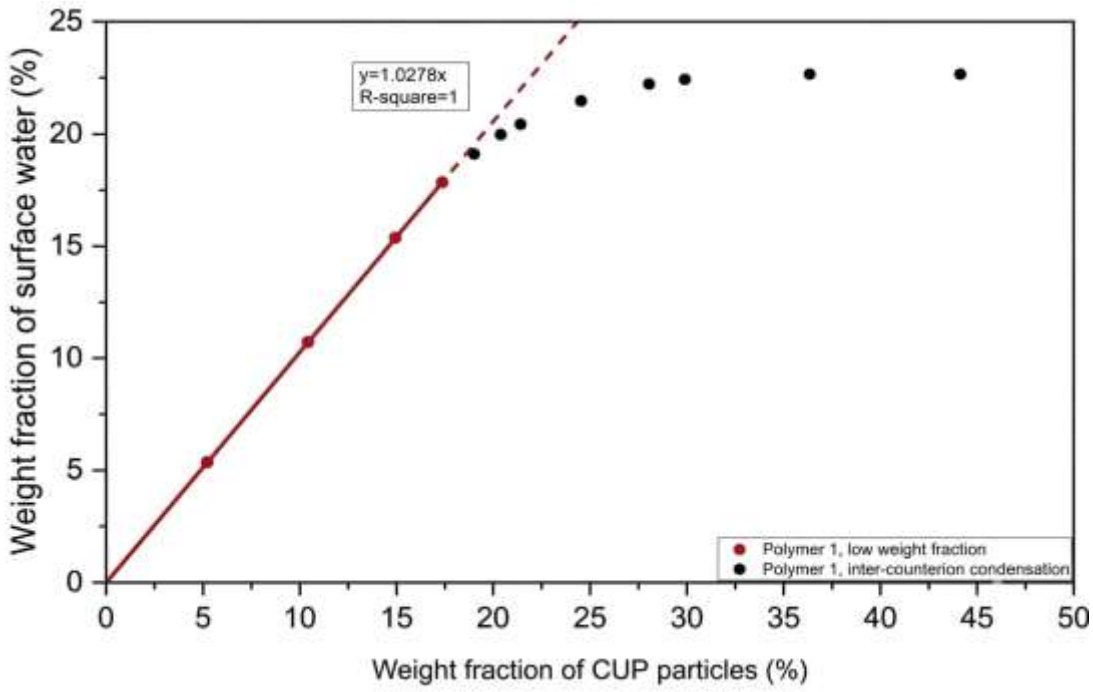


FIG.7. The percentage by weight of water stabilises at around 35 per cent at concentrations above 20 per cent.

**4. Conclusion**

This research investigates the properties of surface water strongly bound to a synthetic monomeric polymer using two techniques: TGA and DSC. The experimental study demonstrated the formation of a surface water layer with a thickness ranging from 0. 45 nm and 0.75 nm, characterised by a density higher than that of free water; this density increases with an increase in surface charge density. This layer possesses a specific heat capacity falling between that of ice and ordinary water, demonstrating that it is constrained and cannot freeze easily-a unique chemical state. It has also been shown that at low polymer concentrations, the proportion of surface water increases to over 20 per cent; this leads to the formation of ion condensation, which in turn reduces the effective charge, resulting in the proportion of surface water remaining stable at approximately 35 per cent, unaffected by cooling. Furthermore, gravimetric measurement results indicated that the presence of polymers accelerates the process of water evaporation; this is due to electrostatic repulsive forces. Compared to confined surface water, it exhibits significant resistance to evaporation and does not evaporate until the water beneath it has dried out. The important practical aspect of this study lies in its potential for use in numerous industrial applications, including improving the quality of water-based coatings by enhancing their stability against freezing and thawing and extending the shelf life of pigments. It can also be applied industrially in water-based inks, in cosmetics, and in pharmaceutical drug delivery systems.

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