# Redox Solution Polymerization of Vinyl Acetate in Mild Conditions and Gel Permeation Chromatography Analysis

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## Abstract

Controlling High Molecular Weight (HMW) governs the suitable process for modeling a wide variety of physico-chemical and rheological properties of polyvinyl acetate (PVAc). To overcome the defects of different polymerization techniques (radical polymerization, reversible termination mechanism, photo-polymerization, reversible addition-fragmentation chain transfer), Amine Peroxide Redox Initiation (APRI) process was launched, involving a bulk organic redox initiator Benzoyl peroxide/Phenyldiethanolamine (Bz2O2 /PhDEA), and methanol as alcoholic solvent, called upon to promote the best performance in highlighting PVAc molecular weight, in mild conditions , at 30°C. PVAc was identified by ATR-FTIR spectroscopy. GPC quantitation was the main tool implemented to identify Molecular Weight Distribution (MWD) of PVAc, in addition to illustration of fractionated PVAc species by Statistica software .Viscometric average weight of PVAc were assessed according to Mark-Houwink Sakurada (MHS) equation from experimental data, results broadly reviewed and confirmed by GPC quantitation.

**Keywords:**-Redox initiation, $Bz_2O_2$/ PhDEA ,PVAc , ATR-FTIR , Viscometry , GPC , Statistica software.

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## 1. Introduction

Since the random birth of Redox Polymerization (RP) in Germany, 1937, first pioneers (R.G.R Bacon, F.A Bovey ,I.M Kolthoff, …) mentioned in well-known references[1-4] highlighted its undeniable assets (ease of application, energy gains, environmental protection) that became vectors of powerful progress in scientific research and technology. New pioneers in RP built the bridge towards setting new concepts of bioactivities where mechanisms of RP play the key role in elucidating and quantifying the level of biological ,chemical, and biochemical phenomenons [5-8].Two landmark dates condition the evolution of RP, the years around 1955 and the years around 1975, which saw a decisive turning point in its history.

These two key dates are synonymous with the passage of Redox Initiation (RI) from the Redox Metal Salts Initiation (RMSI) to the Amine Peroxide Redox Initiation (APRI ) by the use of alkyl or aryl alkyl amines and peroxi-compounds , then the Redox Initiation Systems (RIS) entered the most efficient phase, and the most prolific in its history thanks to the advent of the use of pure organic substances that converted RP to a powerful tool for the synthesis of ecofriendly, biocompatible biomaterials [9-13].APRI highlighted fundamental biological redox metabolisms of life [14,15]. The link between redox exchange and the notion of oxidation under stress is therefore established, which allows the twin sisters Redox Medicine and Redox Biology to now progress at high speed [16,17]. Redox medicine is the new springboard that attracts hundreds of scientists to perform diagnostics technology by implementing redox signaling linked to the appearance of free radicals, via redox biomarkers as key intermediates [18-21].APRI innovation boosted the field of low temperature polymerization (mild polymerization) and opened a wide gate to controlling HMW materials in the range of 0-30°C, the reason that it was propelled to the forefront of sustainable, ecofriendly, non-hazardous process of polymerization [1-3,22-24]. But the biggest challenge in APRI focuses in the great efficiency to improve the chain linearity even by enhancing the macromolecular weight. This characteristic phenomenon highly increases the rheological properties of PVAc without overloading the macromolecular chain by undesirable branching chain. P. Garra et al. [25] and M. Göktaş et al. [26] highlighted the use of Redox Initiating Systems (RIS). According to N. Casado et al. [27], the breakthrough of redox polymers in the energy and medicine sectors gives them access to the activities of biosensors alongside sensitivity to Reactive Oxygen Species (ROS) and Reactive Nitrogen Species (RNS) [28] which are keys intermediates in biological metabolisms, in particular the free radicals formation. Musgrave III et al. [29] , participate in the elucidation of the amine impact nature on the peroxide oxidizer, by proving the superiority of the effectiveness of tertiary arylamines as accelerators reducers compared to alkyl, dialkyl or trialkylamines.

The black box that manages the performances of RP is without any doubt the crucial step of the Trommsdorff–Norrish Effect (TNE) or Gel Effect (GE) [30,31] characterized by its specific parameter Gel Time (GT). The nature of the implemented RIS, and the generated TNE give access to the fundamental properties of the targeted PVAc , in particular the achievement of high molecular weights (HMW) and the improvement of its rheological and physico-chemical properties [32-38]. The tests carried out during this study on the use of Monoethanolamine (MEA), Diethanolamine (DEA), Triethanolamine (TEA) and Dimethylaniline (DMA) as benzoyl peroxide accelerators showed a TNE of varied intensity, particularly in the use of alkylamines, with a fairly reduced GT (on average 2 hours). On the other hand, those carried out with the Bz2O2/ Phenyl diethanolamine (Bz2O2/ PhDEA) system developed a more spread GT (5 hours), a phenomenon which establishes a kinetic control mechanism which conferred better rheological performances, the reasons which motivated our use of Bz2O2/PhDEA during this study [39-41].Many authors highlighted the fundamental role of viscosity in that it constitutes a key database that is able to monitor the rheological materials properties [42,43]. In this context this study provides a set of numerical values of PVAc viscosities via a viscometric analysis ( Ubbelohde), to which is added a more elaborated study based on a GPC analysis of five PVAc macromolecular species (E1,E2,E3,E4,E5) taken from the reaction medium during the mild redox polymerization .Ef is a result sample of mixing E1,E2,E3,E4,and E5, in the same proportions that occurred in the areas (concentrations) of the Waters MWD analysis .Therefore, Ef viscosity is the average viscosities of all the samples taken from the reaction medium.The results of this PVAc MWD make it possible to establish a relationship between the conversion rate, the polymerization time and the viscosity at different stages of the polymerization [21,22,30,31].PVAc is an hydrophobic porous biomaterial. Model development and manufacturing of biomaterials actually needs an iterative process relating to a set based design [29] . The correlation between viscosity, MWD and porosity control the structure-property-function of porous organic materials and constitute an Exploratory Data Analysis (EDA) [44-47] whose exploitation leads to the modeling of porous materials with high-performance properties usable as membranes and bioengineering materials. Therefore, GPC analysis is a key portal in the Machine Learning (ML) and other algorithms that are called to perform porosity and size particles to achieve cutting-edge design of PVAc-based materials [45-47].

## 2.Materials and methods

### 2.1.Materials:

Materials used as Redox Initiators and monomer are described in tables 1and2.

VAc: (Sigma-Aldrich ,Germany, 99 +%) was purified as follows, 200 ml of vinyl acetate were washed with 100 ml of a 10% KOH solution (three times). The monomer is then washed twice with 100 ml of water, and finally dried over MgSO4 for an hour. After filtration, it is distilled at 72.2°C under argon (or N2 atmosphere) at atmospheric pressure, then immediately used [48].

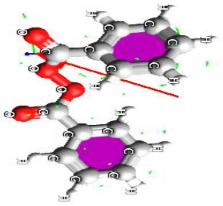
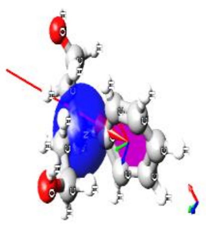
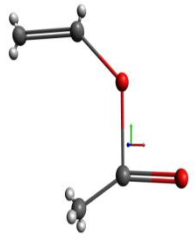
Bz2O2 : (Sigma-Aldrich ,Germany) was recrystallized by dissolving crystals in hot methanol, followed by filtration , then precipitated , step by step , using cold chloroform [11,48 ,49].

PhDEA : (Sigma-Aldrich , Germany) was recrystallized by dissolving crystals in hot ethanol, followed by filtration, then precipitation, step by step, using cold water .The crystals of PhDEA formed are dried at 60° C under vacuum in presence of pentoxide phosphorus P2O5 [11,48 ,49].

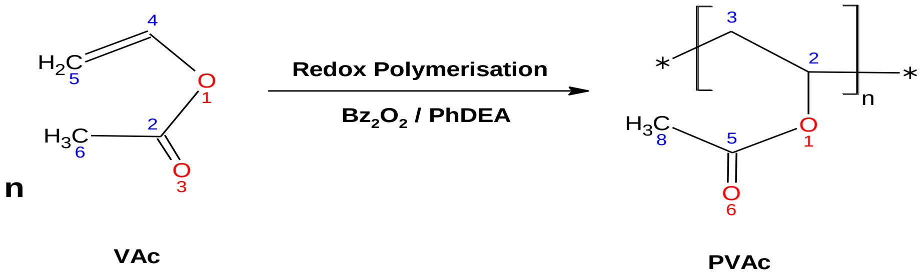
**Table 1. Materials used identification**

| Acronym | Identifiant | Function | Molecular formula | Purity |
|---|---|---|---|---|
| Bz2O2 | IUPAC name: Benzoyl benzenecarboperoxoate<br>Alternative name: Benzoyl peroxide | Initiator | C14H10O4 | ≥ 99% |
| PhDEA | IUPAC name : 2,2'-(phenylazanediyl)di(ethan-1-ol)<br>Alternative name : Phenyldiethanolamine | | C10H15NO2 | ≥ 99% |
| VAc | IUPAC name : Ethenylethanoate<br>Alternative name : Vinyl acetate | Monomer | C4H6O2 | ≥ 99% |

**Table 2. Materials structures**

| Material | Bz2O2 | PhDEA | VAc |
|---|---|---|---|
| 3D<br>Structure |  |  |  |

## 2.2. Vac solution polymerization process:



Scheme 1.VAc  polymerization Equation

Where n is  the polymerization degree of PVAc,  (Scheme 1).

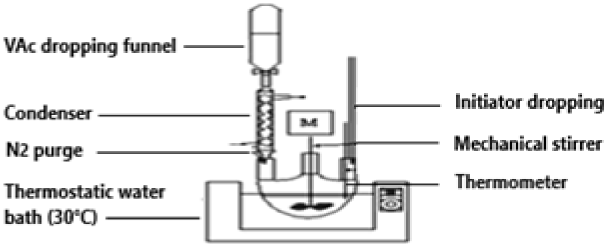


**Figure 1. Reactor of VAc solution polymerization**

Solution polymerization was carried out in a reactor (Figure 1), in absence of oxygen. Purified monomer was placed in a one liter three-necked round bottom glass flask equipped with a glass stirrer, a thermometer, inlet and outlet tubes for nitrogen gas. Solvent methanol was added to the monomer VAc, then the redox initiator Bz2O2/PhDEA was introduced into the medium. The stirred reaction mixture was brought to 5°C by cooling bath, while a stream of nitrogen was circulating through the flask for 15 minutes. At the end of this period, the temperature inside the flask settled to 30°C. Polymerization occurred for nearly 5 hours (in accordance with scheme 1).At the end, polymerization was achieved with a conversion degree of 85 % [50-52 ].

## 2.3 ATR-FTIR characterization

PVAc ATR FTIR spectrum was recorded using a Nicolet 380 Quest ATR Accessory P/N GS10801-B.  A thin film of PVAc was introduced between the anvil and the diamond crystal from the ATR unit to undergo compression .Process of drying occurred at 40°C under vacuum in order to eliminate traces of humidity. Spectrometer was calibrated to run from  500  to 4000 cm-1 .Current optimization protocol set the conditions of scan number and resolution to four scans and 4 cm 1[53-55].

## 2.3. PVAcviscometry

Viscosity of PVAc was the study of many workers due to its great utility in biomedical and industrial applications [56].Specific viscosity was used to determine the reduced viscosity for each sample at experimental temperature. Reduced viscosity is calculated as given equation in table 3.

**Table 3. Equations-types of viscosities**

| Type of viscosity | Equation | Type of viscosity | Equation |
|---|---|---|---|
| Relative viscosity (1) | ɳ = t/t0 | Reducedviscosity (3) | ɳed = ɳ̧p /c |
| Specificviscosity (2) | ɳ̧p = (t-t0)/t0 | Intrinsicviscosity (4) | [ɳ] = limɳ̧p /c<br>c→0 |

### 2.3.1. Calculation of Mv

The Mark–Houwink–Sakurada (MHS) equation (5), [59] gives a relationship between intrinsic viscosity ([ɳ]) and the viscosity average molecular weight , commonly called viscosity average (Mv) . K and {\displaystyle K}a (interaction polymere-solvent parameters) calibrate the equation for each type of polymer, in specific conditions of solvent and temperature. Solvent flow time (t0) and sample flow time (t) were used to calculate intrinsic viscosity [ɳ] by plotting ɳed = f(c){\displaystyle a} , where c is the concentration of the polymer solution in (g/dl).

**Table.4 Experimental viscometric conditions and MHS parameters [57]**

| Material | Solvent | T (°C) | t0 (s) | K | a |
|---|---|---|---|---|---|
| PVAc | Acetone | 20±0.1 | 20.32 | 1.74.10-4 | 0.7 |

t0 (s) is the flow time of acetone solvent [58].

Mv = ([ɳ]/K)1/a(5)

[ɳ]redis deductedusing equations (1,2,3,4) listed in Table 3,and using experimental conditions ,Mark-Houwink parameters, reported in Table 4.Finally, [ɳ] is obtained by extrapolation from plotting ɳed versus concentration c [60-62] . The MHS key equation (5) gave access to viscometricaverage Mv.

## 2.4. Gel permeation chromatography (GPC)

Size exclusion chromatography is called Gel Permeation Chromatography (GPC) [63],when performed using organic solvents , and called Gel Filtration when performed using aqueous solvents , it is a method where separation of different compounds occurs according to their size (hydrodynamic volume) measured by the pores of the stationary phase [64-67] . The main application field of GPC is polymer analysis [68] .

Characterization of PVAc samples was carried out on GPC Waters Millipore according to technical conditions (Table 5). GPC is a chromatographic technique that provides valuable information regarding the molecular weight distribution of a polymer. The columns used for GPC were defined in terms of molecular weight exclusion limit and were normally soft, semi-rigid or rigid gels with varying porosity [69-72] .The molar weight distribution (MWD) of the samples were analyzed at 30 °C using tetrahydrofuran (THF) as an eluent with a flow rate of 0.3 mL.min-1. PVAc MWD samples were estimated using the principle of universal calibration against a polystyrene calibration established using narrow molar mass standards in the range [1000 – 1.500.000] Da.

**Table.5 Experimental GPC conditions**

| | | | | |
|---|---|---|---|---|
| Scale factor 40 | N° of Inj 1 | Max press 200 | ColumnTemp 30°C | Run Time 00.25 |
| Equil Delay 00.05 | Pump Temp 30°C | Sample n° 1 | Inj Temp 30°C | Solvent THF |
| Sensitivity -0.64 | DegasTemp Off | Inj Remain 0 | | |

Six samples were submitted to GPC analysis, five taken from the medium polymerization at different conversion degrees as indicated by Table 8.The sixth sample Ef is a mixture of the five samples E2, E3, E4, E5, E6 .Conversion degrees were calculated by gravimetric method.

## 3.Results

### 3.1. PVAc ATR- FTIR analysis

Infrared spectroscopy is more sensitive in detecting small polar molecules and single bonded chemical compounds such as C–C, C–O and C–H. Therefore, this technique is used in this study for the identification of characteristic bands in our synthetized PVAc material. PVAcATR-FTIR spectra was recorded as seen in Figure 3, in mode transmittance (T %) versus wavenumber (ν). PVAc is mainly characterized by its two strongest C=O stretching vibrational absorption band at 1728 cm-1 and 1222 cm-1 . At 1116 and 1017 cm−1 the symmetric stretching vibrational absorption peaks correspond to the C-O bond in the ester group. (Figure 3, Table 6) [73-77].

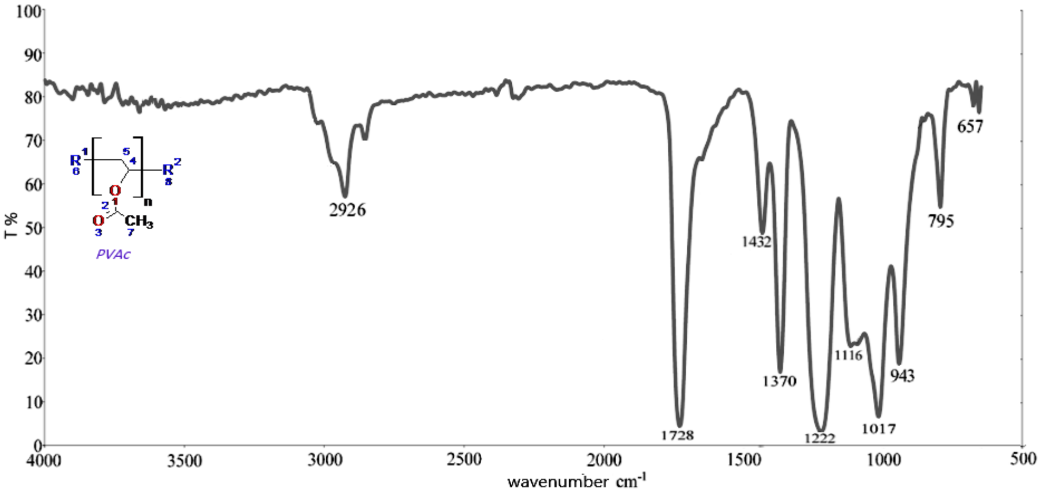


**Figure 3.PVAc ATR- FTIR**

**Table 6.PVAc ATR-FTIR peaks assignments**

| ν(cm-1) | Peak assignment | ν(cm-1) | Peak assignment |
|---|---|---|---|
| 2926 | -CH2- asymmetric stretching (alkyl group) | 943,1017, 1116, 1222 | -C-O- and -C-C- stretching |
| 1728 | -C=O strongest stretching | | |
| 1432 | -CH2 bending | 795 | -C-H- rock |

### 3.2.PVAcViscometry

Tests of viscometryPVAc driven in acetone solution following conditions, at 30°C, using an Ubbelohde viscometer [78-82] immersed in a thermostatic bath led to results plotted as ɳed = f (c). Extrapolation at c = 0 assessed the value of [ɳ] (Figure 4) . It was found that [ɳ] =1.18.

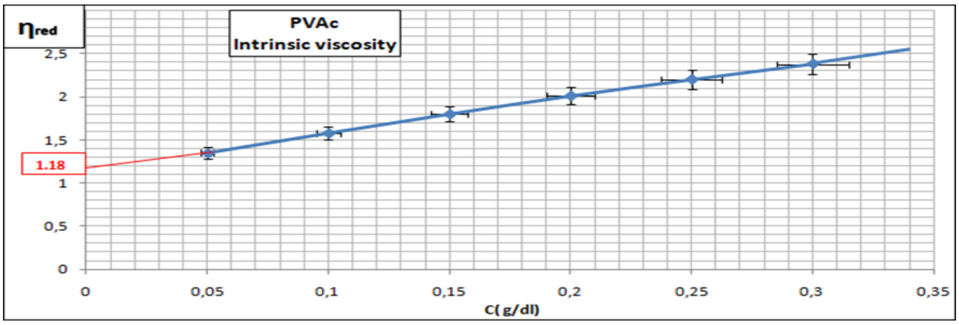


**Figure 4.PVAc Intrinsic viscosity**

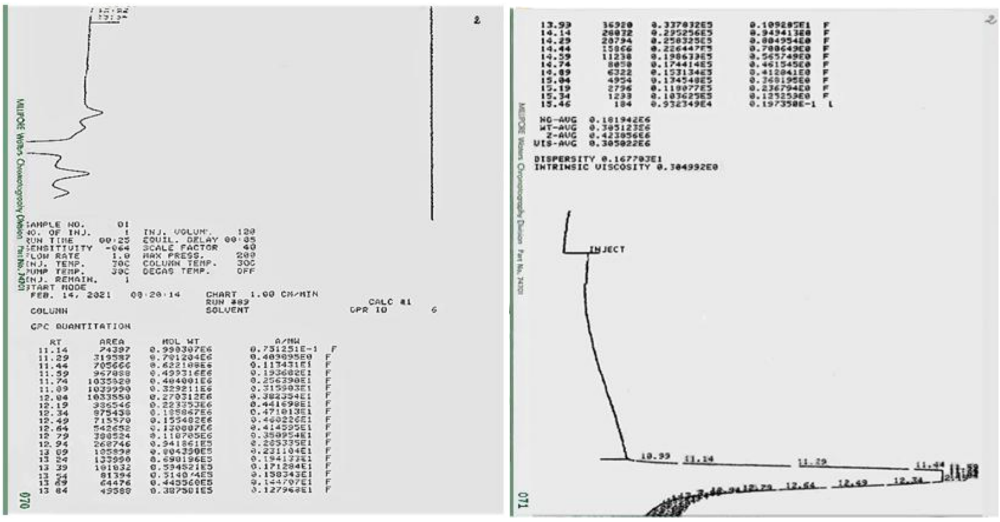
Using Table 4 and HMS equation, we calculated Mv,PVAc,Ubbelhode .Results are reported in Table 7 .

**Table7.PVAcviscometric average**

| Material / Parameter | PVAc |
|---|---|
| [ɳ] | 1.18 |
| Mv,PVAc,Ubbelhode | 2.97.105 |

### 3.3. GPC quantitation:

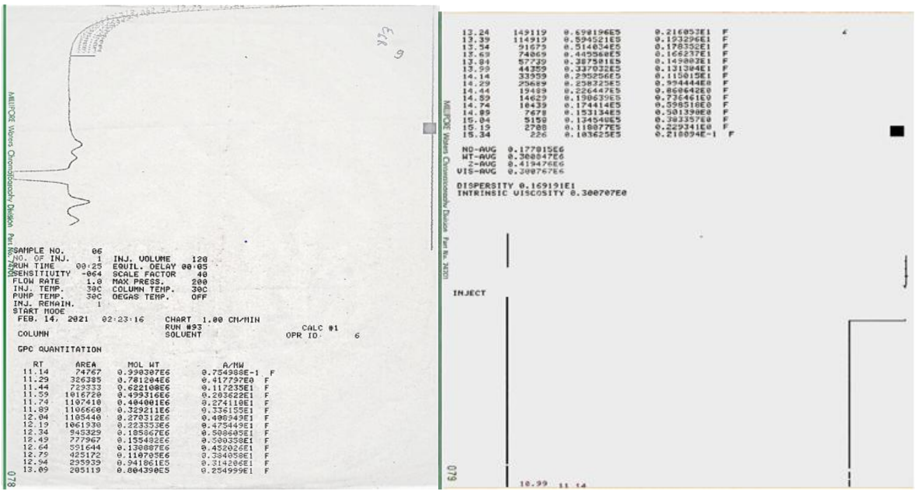
Six samples E2 , E3, E4, E5, E6, Ef taken from the medium at different conversion degrees of polymerisation were subjected to GPC analysis [69, 83] .Ef is the mixed sample of E2, E3,E4,E5,E6 in equal proportion as given by GPC analysis in regard to areas (or concentrations) that remains globally the same through the analysis of the five samples. Following,we present the chromatograms of two particular GPC analysis, E2 GPC and E6 GPC . All the samples [E2-Ef] presented the same MWD at the same RT, only with a slight difference in corresponding areas. Ef represents by its viscosity and mass parameters the original PVAc sample subjected to GPC analysis. In Figure 5 and Figure 6 we present the GPC chromatograms analysis for the samples E2 and E6.



```
SAMPLE NO.       01
NO. OF INJ.       1   INJ. VOLUM.     120
RUN TIME      00:25   EQUIL. DELAY 00:05
SENSITIVITY    -064   SCALE FACTOR     40
FLOW RATE       1.0   MAX PRESS.      200
INJ. TEMP.      30C   COLUMN TEMP.    30C
PUMP TEMP.      30C   DEGAS TEMP.     OFF
INJ. REMAIN.      1
START MODE
 FEB. 14, 2021    08:20:14    CHART  1.00 CM/MIN
                              RUN #89                 CALC #1
 COLUMN                       SOLVENT              GPR ID       6

 GPC QUANTITATION

    RT        AREA      MOL WT            A/MW
   11.14      74397   0.990307E6       0.751251E-1  F
   11.29     319587   0.701204E6       0.403895E0  F
   11.44     705666   0.622108E6       0.113431E1  F
   11.59     967088   0.499316E6       0.193682E1  F
   11.74    1035920   0.404001E6       0.256390E1  F
   11.89    1039990   0.329211E6       0.315903E1  F
   12.04    1033550   0.270312E6       0.382354E1  F
   12.19     986546   0.223353E6       0.441698E1  F
   12.34     875438   0.185867E6       0.471013E1  F
   12.49     715570   0.155482E6       0.460226E1  F
   12.64     542652   0.130887E6       0.414595E1  F
   12.79     398524   0.110705E6       0.359954E1  F
   12.94     268746   0.941861E5       0.285335E1  F
   13.09     185898   0.804390E5       0.231104E1  F
   13.24     133990   0.690196E5       0.194133E1  F
   13.39     101832   0.594521E5       0.171284E1  F
   13.54      81394   0.514044E5       0.158343E1  F
   13.69      64476   0.445560E5       0.144707E1  F
   13.84      49588   0.387501E5       0.127968E1  F
```

```
   13.93      36920   0.337032E5       0.109205E1  F
   14.14      28032   0.295256E5       0.949413E0  F
   14.29      20794   0.258325E5       0.804954E0  F
   14.44      15866   0.226447E5       0.700649E0  F
   14.59      11238   0.198633E5       0.565749E0  F
   14.74       8050   0.174414E5       0.461545E0  F
   14.89       6322   0.153134E5       0.412841E0  F
   15.04       4954   0.134540E5       0.368195E0  F
   15.19       2796   0.118077E5       0.236794E0  F
   15.34       1233   0.103625E5       0.125253E0  F
   15.46        184   0.932349E4       0.197350E-1  L

  MN-AVG  0.181942E6
  WT-AVG  0.305123E6
   Z-AVG  0.423856E6
 VIS-AVG  0.305022E6

 DISPERSITY 0.167703E1
 INTRINSIC VISCOSITY 0.304992E0
```

Figure 5. E2 GPC quantitation



```
SAMPLE NO.       06
NO. OF INJ.       1   INJ. VOLUME    120
RUN TIME      00:25   EQUIL. DELAY 00:05
SENSITIVITY    -064   SCALE FACTOR    40
FLOW RATE       1.0   MAX PRESS.     200
INJ. TEMP.      30C   COLUMN TEMP.   30C
PUMP TEMP.      30C   DEGAS TEMP.    OFF
INJ. REMAIN.      1
START MODE
 FEB. 14, 2021   02:23:16    CHART  1.00 CM/MIN
                             RUN #93                 CALC #1
 COLUMN                      SOLVENT               OPR ID      6

 GPC QUANTITATION

   RT       AREA      MOL WT          A/MW
  11.14     74767   0.990307E6     0.754988E-1  F
  11.29    326385   0.781204E6     0.417797E0  F
  11.44    729333   0.622108E6     0.117235E1  F
  11.59   1016720   0.499316E6     0.203622E1  F
  11.74   1107410   0.404001E6     0.274110E1  F
  11.89   1106660   0.329211E6     0.336155E1  F
  12.04   1105440   0.270312E6     0.408949E1  F
  12.19   1061930   0.223353E6     0.475449E1  F
  12.34    945329   0.185867E6     0.508605E1  F
  12.49    777967   0.155482E6     0.500358E1  F
  12.64    591644   0.130887E6     0.452026E1  F
  12.79    425172   0.110705E6     0.384058E1  F
  12.94    295939   0.941861E5     0.314206E1  F
  13.09    205119   0.804390E5     0.254999E1  F
```

```
  13.24    149119   0.690196E5     0.216053E1   F
  13.39    114919   0.594521E5     0.193296E1   F
  13.54     91679   0.514034E5     0.178352E1   F
  13.69     74069   0.445560E5     0.166237E1   F
  13.84     57739   0.387501E5     0.149003E1   F
  13.99     44359   0.337832E5     0.131304E1   F
  14.14     33959   0.295256E5     0.115015E1   F
  14.29     25689   0.258325E5     0.994444E0   F
  14.44     19489   0.226447E5     0.860642E0   F
  14.59     14629   0.190639E5     0.736461E0   F
  14.74     10439   0.174414E5     0.598518E0   F
  14.89      7678   0.153134E5     0.501390E0   F
  15.04      5159   0.134540E5     0.383357E0   F
  15.19      2708   0.118077E5     0.229341E0   F
  15.34       226   0.103625E5     0.218094E-1   F

  NO-AVG  0.177015E6
  WT-AVG  0.300047E6
   Z-AVG  0.419476E6
 VIS-AVG  0.300767E6

DISPERSITY 0.169191E1
INTRINSIC VISCOSITY 0.300707E0

INJECT
```

Figure 6. E6 GPC quantitation

The GPC results of samples 2 and 6 with respect to MolWt (Mv) and areas are collected in Table 8.

Table 8. Areas and MolWt (Mv) of samples E2 and E6

| RT (mn) | E1 Area | E1 MolWt | E6 Area | E6 MolWt | RT (mn) | E1 Area | E1 MolWt | E6 Area | E6 MolWt |
|---|---|---|---|---|---|---|---|---|---|
| 11.14 | 74397 | 990307 | 74767 | 990307 | 13.39 | 101832 | 59452.1 | 114919 | 59452.1 |
| 11.29 | 319587 | 781204 | 326385 | 781204 | 13.54 | 81394 | 51403.4 | 91679 | 51403.4 |
| 11.44 | 705666 | 622108 | 729333 | 622108 | 13.69 | 64476 | 44556 | 74069 | 44556 |
| 11.59 | 967088 | 499316 | 1016720 | 499316 | 13.84 | 49588 | 38750.1 | 57739 | 38750.1 |
| 11.74 | 1035820 | 404001 | 1107410 | 404001 | 13.99 | 36920 | 33783.2 | 44359 | 33783.2 |
| 11.89 | 1039990 | 329211 | 1106660 | 329211 | 14.14 | 28032 | 29525.6 | 33959 | 29525.6 |
| 12.04 | 1033550 | 270312 | 1105440 | 270312 | 14.29 | 20794 | 25832.5 | 25689 | 25832.5 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 12.19 | 986546 | 223353 | 1061930 | 223353 | 14.44 | 15866 | 22644.7 | 19489 | 22644.7 |
| 12.34 | 875458 | 185867 | 945329 | 185867 | 14.59 | 11238 | 19863.9 | 14629 | 19863.9 |
| 12.49 | 715570 | 155482 | 777967 | 155482 | 14.74 | 8050 | 17441.4 | 10439 | 17441.4 |
| 12.64 | 342652 | 130887 | 591644 | 130887 | 14.89 | 6322 | 15313.4 | 7678 | 15313.4 |
| 12.79 | 388524 | 110705 | 425172 | 110705 | 15.04 | 4954 | 13454.8 | 5158 | 13454.8 |
| 12.94 | 268746 | 94186.1 | 295939 | 94186.1 | 15.19 | 2796 | 11807.7 | 2708 | 11807.7 |
| 13.09 | 165898 | 80439 | 205119 | 80439 | 15.34 | 1298 | 10362.5 | 226 | 10362.5 |
| 13.24 | 13390 | 69019.6 | 149119 | 69019.6 | 15.46 | 184 | 9323.49 | - | 9323.49 |

Thirty macromolecular species were eluted during 04h32mn.The same elution mechanism was repeated for all samples (E2-E6, Ef) .Only areas (concentrations of the samples) observed a slight modification with the advancement of conversion degree.

**Table 9.PVAc GPC RESULTS for E2 -Ef**

| Sample | E2 | E3 | E4 | E5 | E6 | Ef |
|---|---|---|---|---|---|---|
| % conversion | 06.5 | 17.5 | 35.8 | 72.4 | 85.1 | - |
| Mv | 305022 | 303229 | 301369 | 303775 | 300767 | 298743 |
| Mn | 181942 | 174601 | 176656 | 182127 | 177815 | 176587 |
| Mw | 305123 | 303310 | 301413 | 303812 | 300847 | 298820 |

Ef is the mixed sample : Mv, Ef ,GPC = Mv,PVAc,GPC =298743 ( Table 9).

Comparison between PVAcviscometric average(GPC) (Table 9) and PVAcviscometric average ( Ubbelohde ,Table 7 ) is reported in Table 10.

**Table 10.PVAcviscometric averages (GPC and Ubbelohde)**

| Sample | Mv, ,Ef, GPC | Mv,PVAc,Ubbelhode |
|---|---|---|
| PVAc | 298743 | 297000 |

The value Mv,PVAc,Ubbelhode obtained by viscometry is very close to that given by GPC analysis.

## 4. Statisticacomputering of GPC quantitation

All GPC analysis results for samples (E2-E6,Ef,p) were computered in 3D view on Statistica software (Figures 7,8 and 9) [84]:

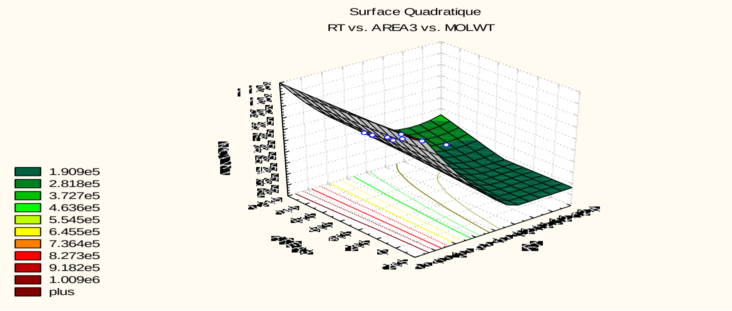


**Figure7. GPC results computered on 3D view (MolWT versus Areas, versus RT)**

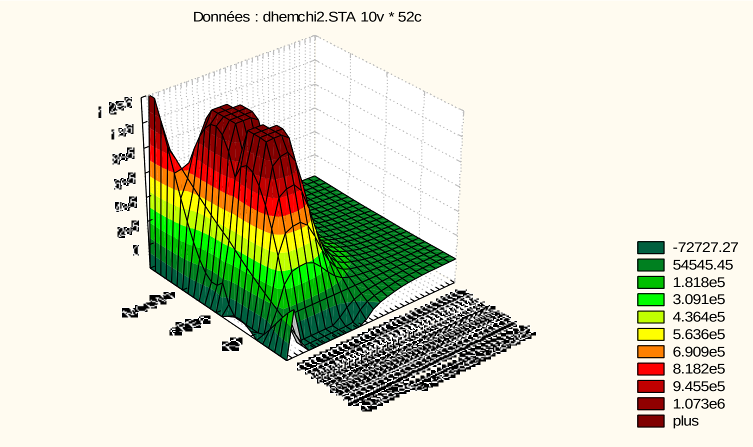


**Figure 8 . GPC results computered on 3D viewSize / MolWt, Areas, RT)**

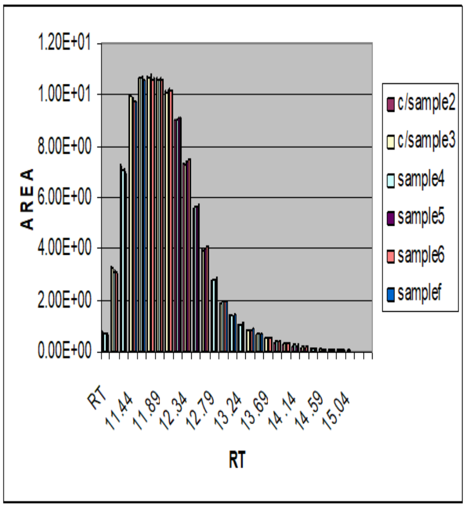


**Figure9 . Area versus RT for six samples**

**Table 11 . Classification of Molecular weight / size**

| Type | size | Mv |
|---|---|---|
| HMW | 🟥 Ultra high | 990307 ≥ Mv ≥ 622108 |
| | V🟨gh | 499316 ≥ Mv ≥ 404.001 |
| MMW | 🟩 High Middle | 404.001 ≥ Mv ≥ 329.211 |
| | 🟩 Middle | 329.211 ≥ Mv ≥ 270312 |
| LMW | 🟩 High Low | 185867≥ Mv ≥ 51403.4 |
| | L🟩 | 51403.4≥ Mv ≥ 10362.5 |
| | V🟩w | Mv ≤ 10.362.5 |

Classification is divided into High Molecular Weight (HMW), Middle Molecular Weight (MMW) and Low Molecular Weight (LMW).Versatility of PVAc covered the fields of Ultra High, High ,Very High, High Middle, Middle, High Low , Low, and Very Low molecular weights as seen in Table11.

## 5. Conclusion

This study provides a set based parameters viscosity, molecular weight, and areas (or concentrations) for six samples accessed via the redox polymerization of VAc, initiated by Bz2O2/PhDEA , through both of viscometry and powerful GPC analysis tool which can control structures, sizes, and physicochemical properties of organic materials.The MWD affects the physical and chemical properties of PVAc, such as its solubility, viscosity, glass transition temperature, thermal stability, mechanical strength, and biodegradability. PVAc HMW and MWD are datasets that power ML for the design of biomaterials.

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## 7. Conflict Of Interest

The authors declare no conflict of interest.

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