VIETNAM JOURNAL OF CHEMISTRY 54(2) 213-216 APRIL 2016
DOI: 10.15625/0866-7144.2016-00263

STUDYING REACTIVITY RATIOS AND PHYSICAL PROPERTIES OF N-VINYL PYRROLIDONE - *N,N'*-DIMETHYLACRYLAMIDE COPOLYMER

Phan Minh Tan[1*], Nguyen Van Khoi[2], Tran Vu Thang[2], Nguyen Van Manh[2], Hoang Thi Phuong[2]

[1]*Viet Tri University of Industry*

[2]*Institute of Chemistry, Vietnam Academy of Science and Technology*

Received 18 January 2016; Accepted for publication 25 April 2016

Abstract

The copolymers of N-vinyl pyrrolidone (VP) and N,N'-dimethyl acryamide (DMAm) were prepared by free radical polymerization in a ethanol solution, using ammonium persulfate (APS)/ascorbic acid (As) as an initiator. The monomer reactivity ratios were calculated by Kelen-Tudos method using elemental analysis data. The characteristics of the copolymer were studied by IR spectroscopy and DSC, TGA methods. The reactivity ratios obtained r_{VP} = 0.195 and r_{DMAm} = 2.62 showed that content of DMAm was higher than VP in the copolymer. In addition, the results showed that the glass transition temperature of copolymer Tg = 98 ^{o}C.

Keywords. Copolymer N-vinyl pyrrolidone-co-N,N'-dimethylacryamide, N-vinyl pyrrolidone, N,N'-dimethylacryamide, acryamide derivatives, copolymerization.

1. INTRODUCTION

Poly(VP-co-DMAm) is widely used in various fields such as vacant land reclamation, erosion, medicines, drilling fluids, paints, adhesives, binders, thickeners, etc…

Alvaro et al. [1] reported a synthesis of poly (VP-co-DMAm) by free radical polymerization in ethanol as the solvent. The reactions were induced thermally at 50^{o}C by using 2,2-azobisisobutyronitrile (AIBN) as a free-radical initiator. The copolymers of acryamide with VP and DMAm with VP were synthesized in dimethylformamide (DMF), with AIBN as the initiator at 60°C for 6 h by B. L. Rivas et al. [2].

In this paper, poly(VP-co-DMAm) was prepared through free radical copolymerization in ethanol, using APS/As as an initiator. Composition of copolymers was determined by elemental analysis and the monomer reactivity ratios were determined at low conversions by Kelen-Tudos method. Characteristics of copolymers were studied by IR spectroscopy and DSC, TGA methods.

2. EXPERIMENTAL

2.1. Materials

The monomers, N-vinyl pyrrolidone (VP), Merck; N,N'-dimethyl acryamide (DMAm), Merck, were distilled in vacuum before used, L-ascorbic acid (As), Merck, ammonium persulfate (APS), Aldrich were re-crystallized from methanol, ethanol 99 %, Merck, diethyl ete 99 %, Merck.

2.2.1. Copolymerization

VP-DMAm copolymer of varying compositions (mole ratio of VP/DMAm: 70/30-30/70) were synthesized by using a solution polymerization technique. Mixtures of monomers VP, DMAm and ethanol were loaded into glass flask connected with agitator, reflux equipment and the temperature was controlled by water bath. During the reaction, the oxygen was removed by nitrogen gas. After raising the temperature to 45 ^{o}C, APS/As (1/1) was loaded and the reaction was started. The reactivity ratios were determined at low conversation of monomer (< 10 %). Products are then separated by precipitation in diethyl ether.

2.2.2. Analysis methods

- Elemental analysis was carried out on Jeol JED 2300 (Japan).
- FTIR analysis of the copolymers was performed in an FTIR Nicolet/Nexus 670 spectrophotometer (USA) between 4000 and 400

cm^{-1} using KBr pellet.

- Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA) of the copolymers was measured by Shimadzu TA-60 Equipment (Japan).

2.2.3. Determination of copolymer composition by elemental analysis [3]

The elemental analysis of copolymer samples with different initial compositions gave the weight percentage (%w/w) of the elements C, H, O and N in the copolymers. Based on those data we calculated the molar fraction of each monomer units in copolymers as described in the following.

The chemical formula of poly(VP-co-DMAm) is $(C_6H_9NO)_x$-$(C_5H_9NO)_y$

The weight percentage (%) of the elements in the copolymers can be calculated through the number of atoms C, H, O and N in VP units (6, 9, 1 and 1) and the corresponding unit in DMAm (5, 9, 1 and 1) as follows:

$$(6x + 5y)M_C = C\% \quad (1)$$
$$(9x + 9y)*M_H = H\% \quad (2)$$
$$(x + y)*M_O = O\% \quad (3)$$
$$(x+y)*M_N = N\% \quad (4)$$

where M_C, M_H, M_O, and M_N are molar mass of carbon, hydrogen, oxygen and nitrogen respectively; C% H%, O% and N% are %w/w of carbon, hydrogen, oxygen and nitrogen obtained from elemental analysis; x and y are the number of moles of VP and DMAm, correspondingly, in 100 g copolymers. Using equations (1), (3) the x and y corresponding to the molar mass and molar percentage of carbon and oxygen were deduced as:

$$x = \frac{C\%}{M_C} - \frac{5O\%}{M_O} \quad (5)$$

$$y = \frac{6O\%}{M_O} - \frac{C\%}{M_C} \quad (6)$$

The mole fraction of VP in poly(VP-co-DMAm) can be determined by equation as follows (7):

$$VP(\%mol) = \frac{x}{x+y} = \left(\frac{C\%}{M_C} - \frac{5O\%}{M_O}\right) \Big/ \frac{O\%}{M_O} \quad (7)$$

2.2.4. Determination of monomer reactivity ratios of VP and DMAm monomer (r_1, r_2)

Copolymer reactivity ratio of VP and DMAm can be determined by Kelen-Tudos (K-T) methods [4].

The equation used for Kelen-Tudos is:

$$\eta = (r_1 + \frac{r_2}{\alpha}) . \xi - \frac{r_2}{\alpha} \quad (8)$$

Where x is the initial mole fraction ratio of the two monomers, $x = \frac{[A]}{[B]}$, y is the mole fraction ratio of two monomers in copolymer, $y = \frac{P_1[A]}{P_1[B]}$;

$$G = \frac{x(y-1)}{y} \text{ and } F = \frac{x^2}{y}$$

$$\eta = \frac{G}{\alpha + F} \text{ and } \xi = \frac{F}{\alpha + F}$$

$$\alpha = \sqrt{F_{max} F_{min}}$$

Plotting the values of η versus ξ provided a straight line that yielded $-r_2/\alpha$ and r_1 as intercepts on extrapolation to ξ = 0 and ξ = 1.

3. RESULTS AND DISCUSSION

3.1. Reactivity ratios

The copolymer composition was determined by elemental analysis method, the results of which are presented in table 1.

Table 1: Composition of VP-DMAm copolymers

Sample	Initial mole fraction ratio VP/DMAm	Elemental analysis data (% w/w)				Copolymer Composition (mole fraction)	
		C	H	O	N	VP	DMAm
M_1	30/70	61.23	8.95	15.91	13.92	0.13	0.87
M_2	40/60	61.45	8.90	15.82	13.84	0.18	0.82
M_3	50/50	61.81	8.81	15.67	13.71	0.26	0.74
M_4	60/40	62.03	8.76	15.58	13.63	0.31	0.69
M_5	70/30	62.48	8.66	15.39	13.47	0.41	0.59

From the determined data on copolymers composition, we used the Kelen-Tudos method to calculate reactivity ratios. The calculated results showed that r_{VP} = 0.195 and r_{DMAm} = 2.622. It is

clearly to note that $r_{VP} < 1$ and $r_{DMAm} > 1$, which means that the reactive capabilities of the R-DMAm$^{\bullet}$ and R'-VP$^{\bullet}$ with DMAm are easier, leading to the copolymers obtained with the composition ratio DMAm/VP ratio higher.

3.2. Characteristics of poly(VP-co-DMAm)

3.2.1. FTIR spectra

The FTIR spectrum of poly (VP-co-DMAm) (mole fraction ratio of 50/50) is presented in Fig 1.

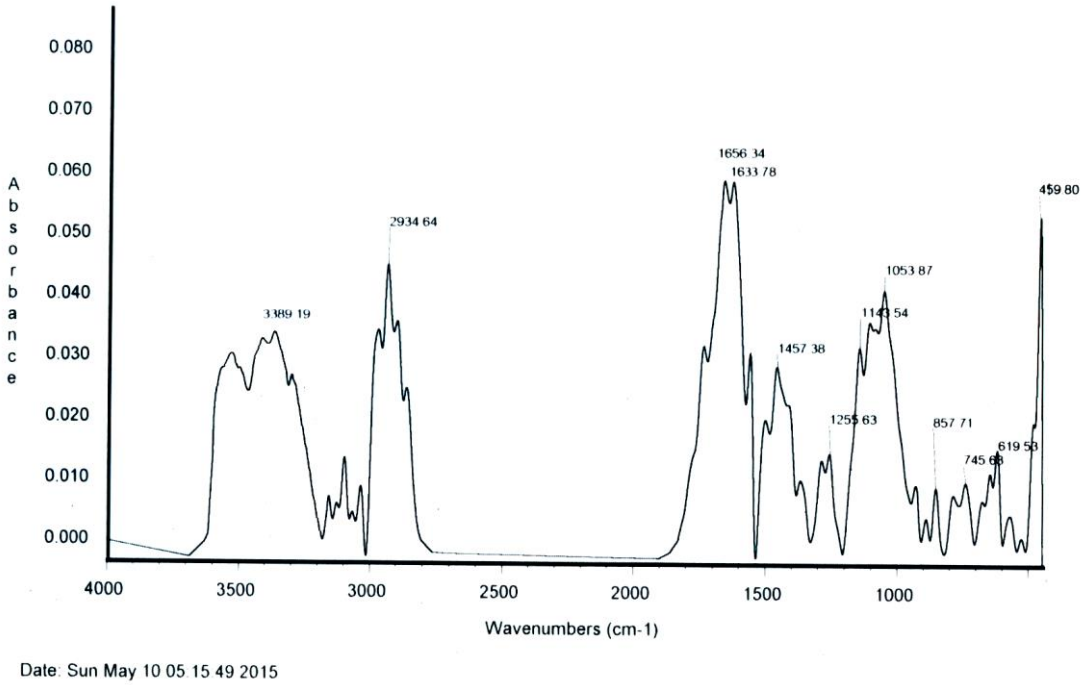

Figure 1: FTIR spectra of poly(VP-co-DMAm) (mole fraction ratio 50/50)

The spectrum shows clearly a broad band at 3398 cm^{-1} assigned to the N-H stretching vibration, following by two intense peaks at 2934 cm^{-1} related to valence fluactation of $–CH_3$ and CH_2 groups. The absorption due to the carbonyl stretching of DMAm and VP units of the copolymer overlap on one another appearing as a broad band in the range of 1656-1633 cm^{-1} and 1255 cm^{-1} that was associated with C-N.

3.2.2. DSC analysis

DSC curves of poly (VP-co-DMAm) are given in figure 2.

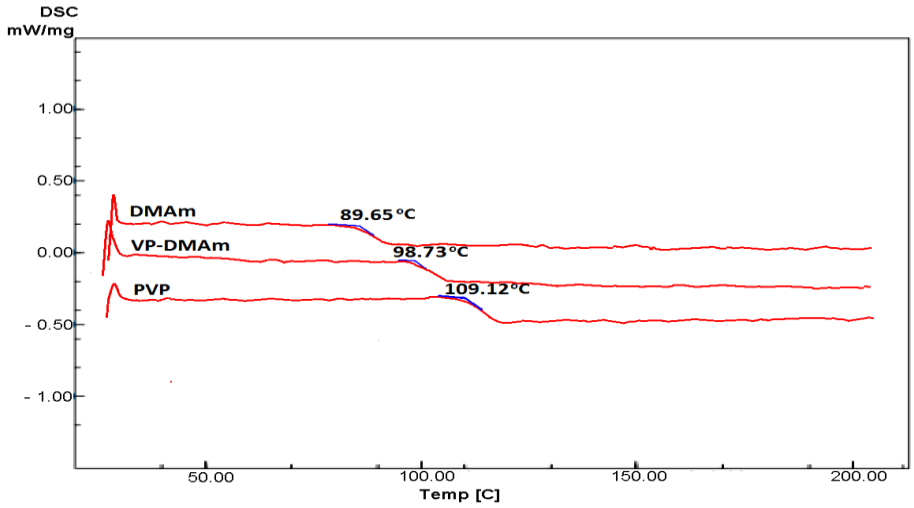

Figure 2: DSC curves of poly(VP-co-DMAm) (mole fraction ratio 50/50)

Figure 2 indicates that, the glass transition temperature (T_g) of poly(VP-co-DMAm) is 98 ^oC, whereas T_g value of polyvinylpyrrolidone (VP) and poly N,N'-dimetylacryamide (DMAm) are 109 ^oC

and 89°C. The T_g values of copolymer lie between T_g values of PVP and PDMAm. In addition, peak Tg poly(VP-co-DMAm) is significantly clear, this demonstrates that the obtained copolymer is free of homonomers.

3.2.3. TGA analysis

The thermogravimetric analysis (TGA) was done to study the thermal decomposition of polymers and also to determine the activation energy for decomposition. TGA curves of poly(VP-co-DMAm) (mole fraction ratio 50/50) are given in figure 3.

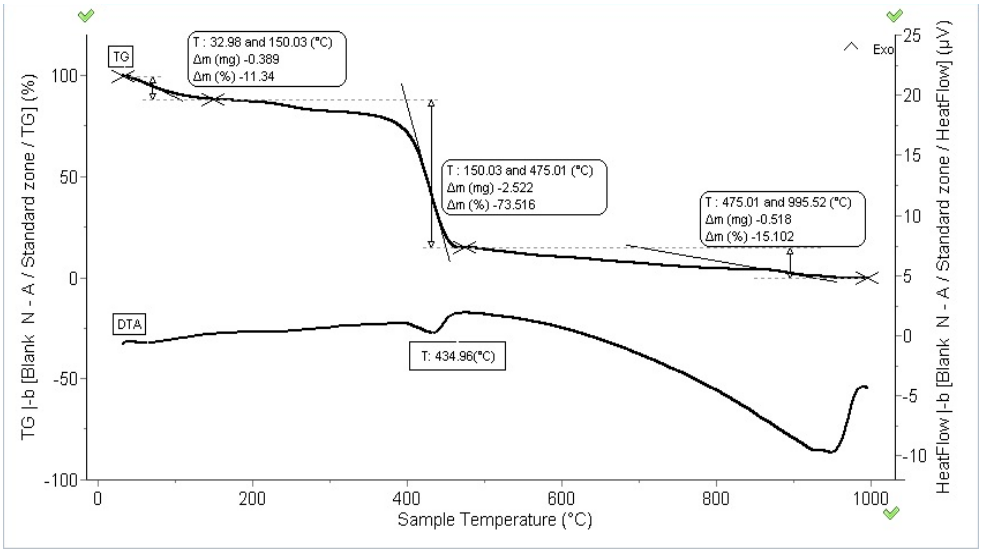

Figure 3: TGA curves of poly(VP-co-DMAm)

The data from figure 3 describes that, the first weight loss at temperatures < 150 °C corresponds to the loss of water in polymer. The second weight loss occurs about 150 to 475 °C is assigned to the water loss due to the formation of molecular internal to decomposition of functional groups C=O and $CO(CH_3)_2$. The third weight loss occurs about 475°C to 995°C originates from cutting of polymer chain generated asphalt, tar.

4. CONCLUSION

Poly (VP-co-DMAm) was prepared through the free radical copolymerization in ethanol, in the presence of $(NH_4)_2S_2O_8$/AS as an initiator. The reactivity ratios of monomers were determined by Kelen-Tudos method using data from elemental analysis. The characteristics of the copolymers were studied by IR spectroscopy, DSC, TGA analysis methods. The results showed that VP has higher reactivity than DMAm (r_{VP} = 0.195 and r_{DMAm} = 2.622), glass transition temperature of copolymer Tg = 98 °C.

Corresponding author: **Phan Minh Tan**
Viet Tri University of Industry
Tien Kien, Lam Thao, Phu Tho
E-mail: minhtanchc@gmail.com.

REFERENCES

1. Alvaro Antonio Alencar de Queiroz, Alberto Gallardo, Julio San RomaHn. *Vinylpyrrolidone - N,N'-dimethylacrylamide water-soluble copolymers: synthesis, physical-chemical properties and proteic interaction*. Biomaterials, **21**, 1631-1643, (2000).
2. B. L. Rivas, S. A. Pooley, M. Soto, K. E. Geckeler. *Water-Soluble Copolymers of 1-vinyl-2-pyrrolidone and Acrylamide Derivatives: Synthesis, Characterization, and Metal Binding Capability Studied by Liquid-Phase Polymer-Based Retention Technique*, J. Appl. Polym. Sci., **72**, 741-750 (1999)
3. Bakhshi H., Zohuriaan-Mehr M. J., Bouhendi H., Kabiri K. *Spectral and chemical determination of copolymer composition of poly(butyl acrylate-co-glycidyl methacrylate) from emulsion polymerization*, Iran Polymer and Petrochemical Institute **28(7)**, 730-736, (2009).
4. Kelen T. and Tudos F. *Copolymerization and determination r_1, r_2 for monomers*, J. Macromol. Sci., **A9**, 1 (1975).