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# STUDYING REACTIVITY RATIOS AND PHYSICAL PROPERTIES OF METHACRYLIC ACID - ETHYL ACRYLATE COPOLYMER

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## ABSTRACT

The copolymerization of methacrylic acid (MAA) and ethyl acrylate (EA) was performed by free radical polymerization in ethanol, in the presence of 2,2-azobisisobutyronitrile (AIBN) as an initiator. The reactivity ratios of monomers were caculatured by Kelen-Tudos method using data from elemental analysis. The charaterstics of the copolymes were studied by IR spectroscopy, DSC, gel permeation chromatography (GPC) and TGA analysis methods. The results showed that MAA has higher reactivity than EA ($r_{MAA}$ = 2.63 and $r_{EA}$ = 0 21), glass transiton temperature of copolyme Tg = 146 °C, the average molecular weight of the copolymers Mw = 251000 (u) and the polydispersity index (PDI) Mw/Mn = 1.70.

*Keywords*: copolymerization, reactivity ratios, methacrylic acid, ethyl acrylate, 2,2-azobisisobutyronitrile.

## 1. INTRODUCTION

Poly(MAA-co-EA)s are widely used in various fields such as paints, adhesives, binders, thickeners, etc.. In the world, many authors have studied on copolymerization between methacrylic and ethylacrylate. Bajaj et al. [1, 2] reported a synthesis of poly(MAA-co-EA) by emulsion polymerization technique, where the copolymer composition was determined by titration methods, elemental analysis and nuclear magnetic resonance (NMR) spectroscopy, the constant of polymerization of polymerization of monomers was determined by Kelen-Tudos method. Bradna et al. [3] studied the effect of pH as well as of concentration and the distribution of EA units in the copolymers to the properties of copolymer.

In this paper, poly(MAA-co-EA) was prepared through free radical copolymerization in ethanol using AIBN as an initiator. Composition of copolymers was determined by elemental analysis and the monomer reactivity ratios were evaluated at low monomer conversions by Kelen-Tudos method. Characteristics of copolymers were studied by IR spectroscopic method and DSC, GPC and thermal gravimetric (TGA) analyses.

## 2. EXPERIMENTAL

### 2.1. Materials

The monomers, methacrylic acid (Merck), ethyl acrylate (Merck) were distilled in vacuum pressure before using. 2,2-azobisisobutyronitrile (AIBN, Aldrich) was re-crystallized from methanol, Etanol 99 % (Merck), Dietyl ete 99 % (Merck), distilled water.

### 2.2. Measurements

*2.2.1. Copolymerization*

MAA-EA copolymer of varying compositions (mole ratio of MAA/EA: 70/30-30/70) were synthesized by using a solution polymerization technique. Mixtures of monomers MAA, EA 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 75 °C, AIBN 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 solution.

*2.2.2. Analysis methods*

- Elemental analysis was recorded on Jeol JED 2300 equipment.

- FTIR spectra of the copolymers were recorded with FTIR Nicolet at Institute of Chemistry, Viet Nam Academy of Science and technology on KBr pellets by a 4000 - 400 $cm^{-1}$ range spectrometer.

- Mass distributions and molar masses of copolymers were determined by GPC method on liquid chromatography system (Shimadzu), LC-10AD-VP pump, RID-10A detector, SPD-10A-VP with THF solution.

- Differential Scanning Calorimetry (DSC) graphs of the copolymers were recorded with Shimadzu TA-60 Equipment.

*2.2 3. Determination of copolymer composition by elemental analysis* [4]

The elemental analysis of copolymer samples with different initial compositions gave the weight percentage (% w/w) of the elements C, H and O 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 fomula of poly(MAA-co-EA) is $(C_4H_6O_2)_x$-$(C_5H_8O_2)_y$.

The weight percentage (%) of the elements in the copolymers can be calculated through the number of atoms C, H and O in MAA units (4, 6 and 2) and the corresponding unit in EA (5, 8 and 2) as follows:

$$(4x + 5y)M_C = C\% \quad (1)$$

$$(6x + 8y)*M_H = H\% \quad (2)$$

$$(2x + 2y)*M_O = O\% \quad (3)$$

where $M_C$, $M_H$, and $M_O$ are molar mass of carbon, hydrogen and oxygen, respectively; C% H%, and O% are %w/w of carbon, hydrogen and oxygen obtained from elemental analysis; x and y are the number of moles of MAA and EA, 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:

$$x = \frac{50\%}{2M_o} - \frac{C\%}{M_c} \tag{4}$$

$$y = \frac{C\%}{M_c} - \frac{2O\%}{M_o} \tag{5}$$

The mole fraction of MAA in poly(MAA-co-EA) can be determined by equation as follows (6):

$$MAA(\%mol) = \frac{x}{x+y} = \left(\frac{50\%}{2M_o} - \frac{C\%}{M_c}\right) \Big/ \frac{O\%}{2M_o} \tag{6}$$

*2.2.4. Determination of monomer reactivity ratios of MAA and EA monomer ($r_1$, $r_2$)*

Copolymer reactivity ratio of MAA and EA can be determined by Kelen-Tudos (K-T) methods [5].

The equation used for Kelen-Tudos is:

$$\eta = (r_1 + \frac{r_2}{\alpha}) . \xi - \frac{r_2}{\alpha} \tag{7}$$

where x is the initial mole fraction ratio of the two monomer, $x = \frac{[A]}{[B]}$

y is the mole fraction ratio of two monomer 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 $\eta$ versus $\xi$ provided a straight line that yielded $-r_2/\alpha$ and $r_1$ as intercepts on extrapolation to $\xi = 0$ and $\xi = 1$.

## 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 MAA-EA copolymers.

| Sample | Initial mole fraction ratio MAA/EA | Elemental analysis data (% w/w) | | | Copolymer Composition (mole fraction) | |
|---|---|---|---|---|---|---|
| | | %C | %H | %O | MAA | EA |
| $M_1$ | 30/70 | 57.69 | 7.49 | 34.82 | 0.585 | 0.415 |
| $M_2$ | 40/60 | 57.30 | 7.39 | 35.31 | 0,.75 | 0.325 |
| $M_3$ | 50/50 | 56.97 | 7.31 | 35.72 | 0.749 | 0.251 |
| $M_4$ | 60/40 | 56.69 | 7.24 | 36.07 | 0.812 | 0.188 |
| $M_5$ | 70/30 | 56.44 | 7.18 | 36.38 | 0.867 | 0.133 |

From the determined data on copolymers composition, we used the Kelen-Tudos method to calculate reactivity ratios. The calculated results showed that $r_{MAA} = 2.63$ and $r_{EA} = 0.21$. It is clearly to note that $r_{MAA} >> 1$ and $r_{EA} << 1$, thus K11> K12 and K22 <K21, which means that the reactive capabilities of the R-MAA$^{\bullet}$ and R'-EA$^{\bullet}$ with MAA are easier, leading to the copolymers obtained with the composition ratio MAA/EA ratio higher than that of the two initial monomer MAA/EA.

### 3.2. Characteristics of poly(MAA-co-EA)

- *FTIR spectra*

The FTIR spectrum of poly(MAA-co-EA) (mole fraction ratio of 50/50) is presented in Figure 1.

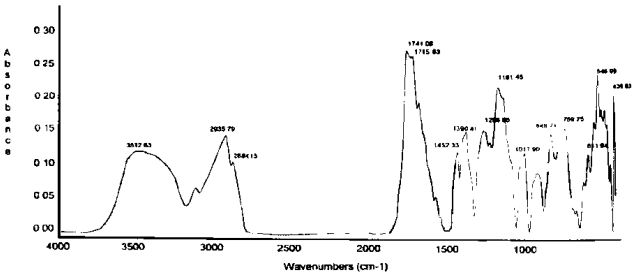


*Figure 1.* FTIR spectra of poly(MAA-co-EA) (mole fraction ratio 50/50).

The spectrum shows clearly a broad band at 3512 $cm^{-1}$ assigned to the –OH stretching vibration, following by two intense peaks at 2935-2884 $cm^{-1}$ related with valence fluactation of $-CH_3$ and $CH_2$ groups. The absorption due to the carbonyl stretching of the acid and ester units of

the copolymer overlap on one another appearing as a broad band in the range of 1715-1741 $cm^{-1}$. The stretching of the ester group is characterized by peak at 1017 $cm^{-1}$.

✓ *DSC analysis*

DSC curves of poly(MAA-co-EA) are given in Figure 2.

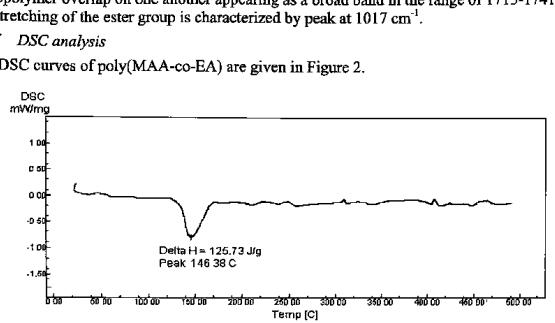


*Figure 2.* DSC curves of poly(MAA-co-EA) (mole fraction ratio 50/50).

Figure 2 indicates that, the glass transition temperature ($T_g$) of poly(MAA-co-EA) is 146.38 °C, whereas $T_g$ value of polymetacrylic axid (PMAA) and polyetyl acrylate (PEA) are 153.56 °C and 119.85 °C [6]. The Tg values of copolymer lie between Tg values of PMAA and PEA. In addition, peak Tg poly(MAA-co-EA) is significantly clear, this demonstrates that the obtained copolymer is free of homonomers.

✓ *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(MAA-co-EA) (mole fraction ratio 50/50) are given in Figure 3.

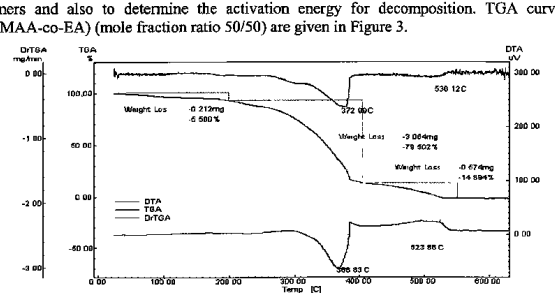


*Figure 3.* TGA curves of poly(MAA-co-EA).

The data from Figure 3 describes that, the first weight loss at temperatures <200 °C corresponds to the loss of water, ethanol and methanol in polymer. The second weight loss occurs at 372.99 °C is assigned to the water loss due to the formation of molecular internal anhydride between adjacent -COOH group or -COOH with O-$C_2H_5$ [6]. The third weight loss occurs at 536.12 °C originates from cutting of polymer chain generated asphalt, tar.

✓ *Molecular weight measurement of poly(MAA-co-EA)*

The GPC was done to determine the molecular weight of the poly(MAA-co-EA) (mole fraction ratio 50/50). The result is shown in Figure 4.

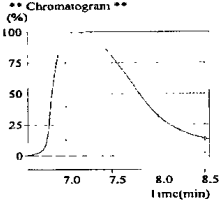


*Figure 4.* GPC curves of poly(MAA-co-EA) (50/50).

The graph demonstrates that the average molecular weight of the obtained copolymers is 251.103 g/mol with polymer dispersion index PDI 1.70, that indicates concentrated distribution of molecular weight.

## 4. CONCLUSION

Poly(MAA-co-EA) was prepared through the free radical copolymerization in ethanol, in the presence of AIBN as an initiator. The reactivity ratios of monomers were computed by Kelen-Tudos method using data from elemental analysis. The charaterstics of the copolymers were studied by IR spectroscopy, DSC, gel permeation chromatography (GPC) and TGA analysis methods. The results showed that MAA has higher reactivity than EA ($r_{MAA}$ = 2.63 and $r_{EA}$ = 0.21), glass transiton temperature of copolymer Tg = 146 °C, the average molecular weight of the copolymers $M_w$ = 251000 (u) and the polydispersity index (PDI) $M_w/M_n$ = 1.70.

## REFERENCES

1. Bajaj P., Goyal M., Chavan R. B. - Synthesis and characterization of Methacrylic acid-Ethyl Acrylate Copolymers, Journal of Applied Polymer Science **53** (3) (1994) 1771-1783.

2. Bradna P., Mrkvičková L., Walterová Z., Quadrat O., Šňupárek J. - Light scattering study of structure of dispersion particles based on ethyl acrylate-methacrylic acid copolymers, Physicochemical and Engineering Aspects **162** (2000) 159-165.

3. Jassal M., Acharya B. N., Bajaj P. - Synthesis, Characterization, and Rheological Studies of Methacrylic Acid–Ethyl Acrylate–Diallyl Phthalate Copolymers, Journal of Applied Polymer Science **89** (5) (2003) 1430-1441.

4. 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) (2009) 730-736.

5. Kelen T. and Tudos F. - Copolymerization and determination $r_1$, $r_2$ for monomers, Journal of Macromolecular Science **A9** (1975) 1.

6. Bajaj P., Meenakshi Goyal, Chavan R. B. - Thermal behavior of methacrylic acid–ethyl acrylate copolymers, Journal of Applied Polymer Science **51** (3) (1994) 423-433.

## TÓM TẮT

### TỔNG HỢP COPOLYME CỦA METACRYLIC AXIT VÀ ETYL ACYLAT: XÁC ĐỊNH HẰNG SỐ ĐỒNG TRÙNG HỢP VÀ MỘT SỐ TÍNH CHẤT CỦA COPOLYME

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Phản ứng đồng trùng hợp của metacrylic axit (MAA) và etyl acrylat (EA) được nghiên cứu bởi quá trình trùng hợp gốc tự do trong dung môi etanol, sử dụng chất khơi mào 2,2-azobisisobutyronitrile (AIBN), với các tỷ lệ mol ban đầu của MAA/EA khác nhau thay đổi từ 30/70 tới 70/30. Hằng số đồng trùng hợp của các monome được tính toán bằng phương pháp Kelen-Tudos sử dụng dữ liệu từ phương pháp phân tích nguyên tố. Đặc trưng tính chất của copolyme được nghiên cứu bởi phương pháp phổ hồng ngoại (IR), phân tích nhiệt vi sai quét (DSC), phân tích nhiệt trọng lượng (TGA) và phương pháp sắc ký thẩm thấu gel (GPC). Kết quả cho thấy MAA có khả năng phản ứng cao hơn EA ($r_{MAA}$ = 2,63 and $r_{EA}$ = 0,21), nhiệt độ thủy tinh hóa của copolyme $T_g$ = 146°C, khối lượng phân tử trung bình (KLPTTB) của copolyme là $251\times10^3$ g/mol và có mức độ phân tán khối lượng phân tử thấp ($M_w/M_n$ = 1,70).

*Từ khóa*: đồng trùng hợp, hằng số đồng trùng hợp, metacrylic axit, etyl acrylat, 2,2-azobisisobutyronitrile.