Aggregation of 2-ethylacrylic acid in dioxane and its effect on the radical copolymerization of maleimide with 2-ethylacrylic acid

Lianjun Shi, Decheng Wan, Junlian Huang*

Department of Macromolecular Science, Fudan University, The Open Laboratory of Molecular Engineering of Polymer, State Education Ministry of China, Shanghai 200433, People’s Republic of China

(Received: April 26, 1999; revised: July 2, 1999)

Introduction

The solvent action in polymerizations is always a very interesting research area. This action might be mainly divided into following categories on the interaction between monomers and solvents: electrostatic forces, hydrogen bonding, and formation of electron donor-acceptor complexes. Some of them, however, are not easy to discern by common technologies such as IR, UV, or NMR. Earlier investigations were mainly focused on the effect of the reaction medium on the reactivity ratios of the monomers.

It is well known that acrylic acid (AA) and methacrylic acid (MAA) can associate in solution via hydrogen bonding. The polymerization of these monomers is strongly dependent on their degree of association. The effect of the reaction medium on the reactivity of these monomers has been extensively investigated.

2-Ethylacrylic acid (EAA) is an interesting monomer, and its polymer, PEAA, shows special biological activity. It is expected that the EAA, like its α-substituted acrylic acid homologues, can also form intermolecular associations via hydrogen bonding. However, the degree of association should be different from AA or MAA due to the steric effect of the ethyl groups. Its copolymerization behavior is scarcely described besides the copolymerization of EAA with styrene (St) and MAA. Moreover, the effect of its intermolecular association in solution on the copolymerization has not been reported up to now.

On the other hand, maleimide (MI) is a very useful monomer. The materials containing MI show heat-resistance and chemical stability. MI copolymers have also been utilized in the pharmaceutical field.

In previous work, the free-radical copolymerization of MI with ethyl α-phenylacrylate and ethyl α-hydroxy-
methacrylate\textsuperscript{16} were investigated, respectively. Copolymers with alternating structure for the former and random structures for the latter were obtained. The electron-donating property of the phenyl-substituted acrylate and the electron-attracting property of the hydroxymethyl-substituted acrylate may play an important role in determining the copolymerization mechanism and the copolymer structure.

In the present work, our interests are focused on the intermolecular association of EAA molecules via hydrogen bonding and its effect on the copolymerization of EAA with MI.

**Experimental part**

**Materials**

Diethyl malonate (Shanghai Third Reagent Factory, China) was purified by distillation at reduced pressure. The fraction of 82 °C/7 mmHg was collected. Maleic anhydride (Shanghai Third Reagent Factory) and urea (Wuxi Mingfeng Reagent Factory) were used as obtained. AIBN was recrystallized from methanol. All other reagents were purified by standard methods.

**Monomer preparation**

2-Ethylacrylic acid (M\textsubscript{2}) was obtained by hydrolysis of ethyl 2-ethylacrylate (EEA) in an ethanol solution of potassium hydroxide. EEA was prepared following procedures described by Atta-Ur-Rahman\textsuperscript{17} and Penelle\textsuperscript{18} and purified twice by distillation at reduced pressure yielding of 46%.

\textsuperscript{1}H NMR (CDCl\textsubscript{3}): \( \delta = 5.64 \) (s; 1H, trans-H of \(-CH\textsubscript{2}\)), \( \delta = 6.30 \) (s; 1H, cis-H of \(-CH\textsubscript{2}\)), \( \delta = 2.30 – 2.37 \) (m; 2H, \(-CH\textsubscript{2}\)), \( \delta = 1.08 – 1.13 \) (t; 3H, \(-CH\textsubscript{2}\)), \( \delta = 11.44 \) (broad peak; 1H, \(-COOH\)).

IR: \( \nu = 1697 \) (\( \text{C} = \text{O}\)), \( \nu = 1629 \) (\( \text{C} = \text{C}\)), \( \nu = 948 \) (\( \text{OH}\)), \( \nu = 3500 – 2500 \) cm\textsuperscript{-1} (\( \text{COOH}\)).

MI (M\textsubscript{1}) was prepared as reported previously\textsuperscript{19}. The m.p. of the product recrystallized from ethyl acetate was 93 – 94 °C. It was further purified by sublimation under vacuum prior to use.

\textsuperscript{1}H NMR (dimethyl sulfoxide (DMSO)-d\textsubscript{6}): \( \delta = 10.9 \) (s; 1H, \(-NH\)), \( \delta = 6.9 \) (s; 2H, \(-CH\textsubscript{2}\)).

**Copolymerization**

The accurately weighed MI, EAA, and AIBN and a given amount of dioxane were added into a 100-mL glass ampoule, degassed three times by freeze-pump-thaw cycles at 77 K and sealed off under N\textsubscript{2}. The copolymerization reactions with different monomer feed ratios were performed at 60 °C ± 0.1 °C. After a given time, the ampoules were removed from the oil bath and the contents were poured into a large excess of diethyl ether. The precipitants were purified with diethyl ether in a Soxhlet extractor for 24 h. The homopolymers of 2-ethylacrylic acid and MI were obtained by conventional radical polymerization.

**Polymer characterization**

\textsuperscript{1}H NMR spectra were recorded on a Bruker MSL-300 spectrometer with tetramethylsilane (TMS) as internal standard and DMSO-d\textsubscript{6} as solvent. IR spectra were scanned by a Magna-550 FTIR spectrometer. Thermogravimetric data were obtained by using a NETZSCH TG 209 thermal analyzer in a nitrogen atmosphere at a heating rate of 10 °C/min. Elemental analyses were carried out by a Carlo Erba 1106 elemental analyzer.

**Viscosity measurements**

Viscosity measurements on EAA in dioxane were carried out at 25 °C ± 0.1 °C using an Ubbelohde viscometer with a capillary diameter of 0.49 mm. Measurements of each concentration were repeated three or four times.

**Results and discussion**

**Synthesis and characterization of poly(MI-co-EAA)**

The copolymerization of MI with EAA was carried out in dioxane at 60 °C under the constant total monomer concentration of 8 mol/L and low conversion (less than 10%). The copolymerized product is a white powder and soluble in methanol, ethanol, dimethylformamide (DMF), DMSO, and dioxane (DIO). Both, poly(EAA) and poly(MI), however, are not soluble in dioxane.

The IR spectra of the copolymers shows the characteristic bands of MI and EAA, at 2 977 cm\textsuperscript{-1} (\( \text{CH}_2\)) and 1 712 cm\textsuperscript{-1} (\( \text{C} = \text{O}\)) attributed to the EAA component, and 1 774 cm\textsuperscript{-1} (\( \text{C} = \text{O}\)) attributed to the imide group of MI. The \textsuperscript{1}H NMR spectrum of the copolymer shown in Fig. 1 indicates the proton signals of the carboxylic acid group of EAA at 12.6 ppm and the imide group of MI at 11 ppm, respectively.
As it was mentioned before, acrylic acid and its homologues can aggregate in solvents due to the formation of intermolecular hydrogen bonds. The reactivity of dimers, trimers and oligomers are greater than that of a single acrylic acid molecule. In our system, however, the case is more complicated: The MI can constitute contact-CTC with EAA, EAA can aggregate by itself and dioxane can form complexes with EAA. Therefore the copolymerization of MI and EAA depends on the results of these interactions.

The presence of multimolecular aggregates have been proven by viscosity measurements\cite{6,8}. Fig. 2 shows the relationship between the mole fraction of EAA in dioxane and the flow time. It is obvious that the longer the flow time, the higher the viscosity of the system. It was observed that the flow time of the system increases with the EAA mole fraction and reaches a maximum, then decreases slowly. This indicates that the degree of association of EAA increases with the mole fraction of EAA in solution. The maximum degree of aggregation is reached for a mole fraction of EAA of about 75%. Champiro\cite{6} found a similar behavior in investigations concerning the molecular association of acrylic acid.

The interaction between EAA and dioxane can be determined by IR spectroscopy. Fig. 3(A) shows the associated carboxyl stretching frequency of EAA at 1697 cm\(^{-1}\). When the EAA was diluted with dioxane, a new peak at 1721 cm\(^{-1}\) (B) appeared beside the former peak. If the concentration of EAA was dropped continuously, the peak at 1697 cm\(^{-1}\) weakened and the peak at 1721 cm\(^{-1}\) strengthened simultaneously (C, D). If the concentration of EAA reached about 2 mol/L, as shown in Fig. 3(E), the associated carboxyl peak at 1697 cm\(^{-1}\) almost disappeared and only the peak at 1721 cm\(^{-1}\) was left. Therefore the aggregates of EAA molecules and the interaction between EAA and dioxane can be described using following equations:

\[
\begin{align*}
\text{HO} & - \text{C} \equiv \text{O} \quad \text{HO} & - \text{C} \equiv \text{O} \\
\text{HO} & - \text{C} \equiv \text{O} & \text{HO} & - \text{C} \equiv \text{O} \\
\end{align*}
\]

Fig. 2. Relation of flow time with the molar fraction of EAA in dioxane.

Fig. 3. IR spectra of EAA in dioxane solutions of different concentrations: (A) without solvent, (B) 6.2 mol/L, (C) 4.1 mol/L, (D) 3.5 mol/L, (E) 2.0 mol/L.
**Monomer reactivity ratio and copolymer microstructure**

The reactivity ratios $r_1$ and $r_2$ for the monomers MI and EAA, respectively, were evaluated by the Kelen-Tudos method \(^{20}\) at low conversions using following linear equation:

$$\eta = r_1 \xi - r_2 (1 - \xi)/a$$

where:

$$\eta = X (Y - 1)/a Y + X^2, \xi = X^2/a Y + X^2, X = [M_1]_0/[M_2]_0$$

$$Y = d[M_1]/d[M_2], \ a = [(X^2/Y)_{\text{max}}(X^2/Y)_{\text{min}}]^{1/2}, [M_1]_0, [M_2]_0$$

and $d[M_1], d[M_2]$ are the initial and the instant concentrations of MI and EAA, respectively. The ratios $r_1$ and $r_2$ obtained by graphical evaluation (Fig. 4) are 0.07 and 1.00, respectively.

![Kelen-Tudos plot for the determination of the monomer reactivity ratios for the MI-EAA copolymerization system](image)

Fig. 4. Kelen-Tudos plot for the determination of the monomer reactivity ratios for the MI-EAA copolymerization system

The copolymer compositions for the different feed ratios were determined by elemental analysis, which is listed in Tab. 1. The average composition curve shown in Fig. 5 was drawn using the classical Lewis-Mayo copolymerization equation \(^{21}\). The experimental composition data fits well with the theoretical curve. The product $r_1 \cdot r_2 = 0.07$ indicating that the copolymerization of MI and EAA shows a strong alternating tendency by the formation of contact CTC \(^{22}\). However, as shown in Fig. 5 and Tab. 1, in most cases the copolymer composition deviates greatly from 50:50 except for the case of the 80:20 feed ratio for MI/EAA. It was found that when the content of MI in the feed ratio was less than 20%, the copolymer composition was nearly the same as the feed ratio; when the content of MI in the feed ratio was greater than 20% (it varied from 20% to 90%), the MI in the copolymer only alternated from 20% to 60%. The increase of MI in the copolymer was much slower than that in the feed ratio. If the MI content in the feed ratio was more than 90%, the MI in the copolymers increased greatly again. In order to elucidate the above-mentioned experimental phenomena, the statistical distribution of the monomer sequences, MI-MI, EAA-EAA, and MI-EAA are calculated using the following equations \(^{23}\):

$$X = \phi_1 - 2\phi_3 (1 - \phi_1)/(1 + [(2\phi_1 - 1)^2 + 4 r_1 \cdot r_2 \phi_1 (1 - \phi_1)]^{1/2})$$

$$Y = (1 - \phi_3) - 2\phi_3 (1 - \phi_1)/(1 + [(2\phi_1 - 1)^2 + 4 r_1 \cdot r_2 \phi_1 (1 - \phi_1)]^{1/2})$$

$$Z = 4\phi_1 (1 - \phi_3)/(1 + [(2\phi_1 - 1)^2 + 4 r_1 \cdot r_2 \phi_1 (1 - \phi_3)]^{1/2})$$

where $r_1$ and $r_2$ are the reactivity ratios of MI and EAA, respectively. $\phi_1$ is the molar fraction of MI in the copolymer, which is obtained from elemental analysis. $X$, $Y$, and $Z$ are the mole fractions of the MI-MI, EAA-EAA, and MI-EAA sequences in the copolymer, respectively. The experimental data are listed in Tab. 2, from which it can be observed that when the MI content in the feed ratio was less than 20%, MI-MI sequence in copolymers is

---

**Tab. 1.** Radical copolymerization of MI (M<sub>1</sub>) with EAA (M<sub>2</sub>) in dioxane with AIBN as an initiator at 60 °C

<table>
<thead>
<tr>
<th>Run No.</th>
<th>MI in feed mol-%</th>
<th>Copolymer composition</th>
<th>Conversion %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>1.41</td>
<td>10.00</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>2.48</td>
<td>17.60</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>3.47</td>
<td>24.60</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>4.52</td>
<td>32.00</td>
</tr>
<tr>
<td>5</td>
<td>70</td>
<td>6.24</td>
<td>44.00</td>
</tr>
<tr>
<td>6</td>
<td>80</td>
<td>7.23</td>
<td>50.90</td>
</tr>
<tr>
<td>7</td>
<td>90</td>
<td>8.99</td>
<td>63.00</td>
</tr>
</tbody>
</table>

a) \([\text{AIBN}] = 4.8 \times 10^{-2} \text{mol/L}, [\text{M}_1]_0 + [\text{M}_2]_0 = 8 \text{mol/L.}\)

b) The average nitrogen content in the copolymer was obtained by duplicate analysis.

---

**Fig. 5.** Monomer-copolymer composition diagram of the copolymerization of MI with EAA. The solid line corresponds to the theoretical diagram calculated by reactivity ratios: $r_{\text{MI}} = 0.07$, $r_{\text{EAA}} = 1.0$
In this case, MI constitutes comonomers with EAA, and is then copolymerized. The MI content of MI-MI sequences in the copolymer was attributed to the low homopolymerization rate constant of MI. For example, when MI in feed ratio was varied from 20 to 80%, the MI-MI sequences in the copolymers increased only from 0.3 to 11.4%, but the content of alternating MI-EAA sequences varied from 34.5 to 79.0%. The low content of MI-MI sequences in the copolymer was attributed to the low homopolymerization rate constant of MI ($\alpha = 0.07$).

Now we can explain the plot of feed ratio vs. copolymer composition shown in Fig. 5. When the content of MI in the feed ratio is less than 20%, i.e., the corresponding EAA concentration is high, dimers, trimers and aggregates composed of many EAA molecules might be formed. In this case MI constitutes comonomers with aggregates of EAA, and is then copolymerized. The MI content in the copolymers is only dependent on the number of EAA molecules in the aggregates which constituted comonomers with MI, and is independent of the monomer feed ratio. This explains the MI content in the copolymers is being higher than that in the feed ratio and at the same time the copolymer composition sharply deviating from 50:50. When the MI content in the feed ratio is increased, i.e., the concentration of EAA in dioxane decreases, the aggregates will dissociate into single monomers due to the intermolecular hydrogen action between EAA and dioxane. MI will constitute comonomers with single EAA molecules, rendering the alternating copolymerization tendency stronger than before. When the MI content in feed ratio is more than 90%, i.e., the EAA concentration in dioxane is rather dilute, the MI not only copolymerizes with single EAA molecules via the alternating mode, but also polymerizes by itself after EAA is consumed. That is the reason why the MI content in the copolymers increases considerably in this stage.

### Effect of monomer dilution on copolymerization
It is well known that $\alpha$-substituted acrylates$^{18,24}$ have a relatively low ceiling temperature ($T_c$), for example the $T_c$ of methyl 2-ethylacrylate is only 82°C. Furthermore the dilution of monomer makes the $T_c$ to decrease$^{25}$. If the polymerization of a monomer is conducted at a temperature close or higher than its corresponding $T_c$, the terminal units of the polymer formed will be prone to depolymerize. In order to derive reliable conclusions whether detectable depolymerization occurred or not in our system, the effect of monomer dilution with a fixed feed ratio on the copolymerization was preformed. If the depolymerization occurs, the EAA content in the copolymer should drop as the concentration of EAA decreases, because the $T_c$ also decreases with the dilution of the monomers$^{25}$. In our experiment, however, the EAA content in the copolymer, did not change with the decrease of the initial EAA concentration, as shown in Table 3. Its value is in the range of 43 – 44.4 mol-%, although the EAA concentration varied from 0.4 to 2.4 mol/L. We also observed that the viscosity of the copolymers made from different concentrations of EAA with fixed feed ratio [MI/EAA (mol/mol): 7/3] is nearly the same. Therefore, the copolymer composition in this copolymerization system is mainly dependent on the feed ratio and independent of the monomer concentration. It provided strong evidence that no depolymerization is operative in our system.

### Thermal stability of the poly(MI-co-EAA)
The thermal stability of the copolymers was studied by programmed thermogravimetric (TG) analysis over a temperature range from 20°C to 600°C under a nitrogen atmosphere. Typical TG curves for the copolymers are given in Fig. 6. The thermal behaviors of poly(EAA) and the copolymers with different compositions are summit-
ized in Tab. 4, where $T_i$ designates the initial decomposition temperature, $T_{\text{max}}$ the temperature of the maximum rate of weight loss, and $T_f$ the final decomposition temperature. It was found that if the EAA content in the copolymers is less than 37%, only a one-step degradation process can be detected. If the EAA content in copolymers is higher than this value, a two-stage degradation is observed. Fig. 7 shows the IR spectra of the copolymer samples with different composition before and after heating in a nitrogen atmosphere from 100°C to 260°C. It was found that if the EAA content in the copolymer is less than 37%, no structural changes can be observed after heating the copolymer as shown in Fig. 7 (A) and (B). When the EAA content in the copolymers is higher than 37%, their spectra almost kept their original appearance except for an increase of the peak intensity at 1036 cm$^{-1}$ (Fig. 7 (C)). Obviously the copolymer color did not change. When the EAA content in the copolymers was higher than 56% (Fig. 7 (D)), new bands appeared. These peaks at 1803 cm$^{-1}$, 1756 cm$^{-1}$, and 1036 cm$^{-1}$ are assigned to anhydride. The copolymer’s color turned from pale to light yellow. The higher the EAA content in the copolymer, the weaker the peak at 1712 cm$^{-1}$ for the carboxyl groups and the stronger the peaks attributed to the anhydride (Fig. 7 (E), (F) and (G)). In order to explain the experimental facts clearly, the mean sequence lengths of successive MI-MI ($l_1$) and EAA-EAA structures ($l_2$) in the copolymers, calculated by the following equations$^{23}$, are introduced:

$$l_1 = 1 + r_1 \left[ M_1 \right]_0 \left[ M_2 \right]_0$$
$$l_2 = 1 + r_2 \left[ M_2 \right]_0 \left[ M_1 \right]_0$$

(Here $l_1$ and $l_2$ represent mean sequence lengths of successive MI-MI and EAA-EAA structures in the copolymer,

Tab. 3. Influence of EAA concentration in the feed on its content in corresponding copolymer at 60°C in dioxane$^a$

<table>
<thead>
<tr>
<th>EAA concentration mol/L</th>
<th>Conversion %</th>
<th>N content in copolymers %</th>
<th>EAA content in copolymers mol-%</th>
<th>$[\eta]$ cm$^{-1}$ g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.4</td>
<td>9.12</td>
<td>6.24</td>
<td>44.0</td>
<td>21.39</td>
</tr>
<tr>
<td>1.5</td>
<td>9.06</td>
<td>6.2</td>
<td>43.7</td>
<td>19.03</td>
</tr>
<tr>
<td>1.0</td>
<td>5.44</td>
<td>6.1</td>
<td>43.0</td>
<td>–</td>
</tr>
<tr>
<td>0.75</td>
<td>3.64</td>
<td>6.2</td>
<td>43.7</td>
<td>18.73</td>
</tr>
<tr>
<td>0.6</td>
<td>1.85</td>
<td>6.3</td>
<td>44.4</td>
<td>–</td>
</tr>
<tr>
<td>0.5</td>
<td>3.19</td>
<td>6.3</td>
<td>44.4</td>
<td>19.56</td>
</tr>
<tr>
<td>0.4</td>
<td>1.15</td>
<td>6.2</td>
<td>43.7</td>
<td>–</td>
</tr>
</tbody>
</table>

$^a$ $M_1/M_2$ (mol/mol) = 7:3, [AIBN] = $4.8 \times 10^{-2}$ mol/L.

$^b$ The average nitrogen content in copolymer was obtained by duplicate analysis.

$^c$ Intrinsic viscosity [$\eta$] in DMF at 30°C.

Tab. 4. Thermal behavior of copolymers and homopolymers

<table>
<thead>
<tr>
<th>Copolymer composition MI mol-%</th>
<th>First stage</th>
<th>Second stage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_i$ °C</td>
<td>$T_{\text{max}}$ °C</td>
</tr>
<tr>
<td>63.0</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>50.9</td>
<td>220</td>
<td>247</td>
</tr>
<tr>
<td>44.0</td>
<td>216</td>
<td>232</td>
</tr>
<tr>
<td>32.0</td>
<td>198</td>
<td>217</td>
</tr>
<tr>
<td>24.6</td>
<td>187</td>
<td>212</td>
</tr>
<tr>
<td>17.6</td>
<td>190</td>
<td>215</td>
</tr>
<tr>
<td>10.0</td>
<td>180</td>
<td>200</td>
</tr>
<tr>
<td>0</td>
<td>180</td>
<td>218</td>
</tr>
</tbody>
</table>

Fig. 6. Typical TG curves of the MI-EAA copolymers and homopolymers: (▲) poly(MI), (●) EAA: 37%, (▲) EAA: 68%, (+) EAA: 82.4%, (○) poly(EAA)

![Temperature, °C](image)

![Weight Loss, %](image)
$r_1$ and $r_2$ are the monomer reactivity ratios for MI and EAA, respectively; $[M_1]_0$ and $[M_2]_0$ are the initial concentration of MI and EAA. When the EAA content in the copolymer is smaller than 37%, the copolymer with the alternating structure, shown in Fig. 5, was formed. The mean sequence length of successive EAA-EAA units listed in Tab. 2 is smaller than 1.5, so the intramolecular dehydration between the carboxyl groups of the EAA units in the copolymer is difficult to carry out. A change of the chemical structure or the weight loss of the copolymer was also not observed, even when heated up to 260°C. However, when the EAA content in the copolymer is higher than 37%, the copolymer composition gradually deviates from the alternating structure, and the mean sequence length ($l_2$) of successive EAA-EAA structures is higher than 2.00. The intramolecular dehydration of these copolymers, resulting in six-membered anhydride rings, occurs easily, and the weight loss increases considerably. This process can be described using the following chemical equation:

\[
\begin{align*}
\text{C}_6\text{H}_{10}\text{O}_2 \quad \text{O} \quad \text{H}_2\text{O} \quad \text{heat} \quad \text{C}_6\text{H}_{10}\text{O}_2 \\
\text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O}
\end{align*}
\]

As for the copolymer samples in the second stage, it is no longer soluble in any solvent. The crosslinking net might be formed via the intermolecular dehydration between carboxyl groups of EAA and imide of MI and between carboxyl groups of different macromolecules.

Tab. 5 lists the degradation activation energy of the copolymers, which was calculated by Broido’s method. It shows that the activation energy drops with the decrease in the EAA content in the copolymers, which
may be attributed to the decrease of inter- and intramolecular association of carboxyl groups of the copolymers.

Acknowledgement: We appreciate the financial supports from the Natural Science Foundation of China and the Doctor Training Foundation of the State Education Ministry of China.

5) I. Sideridoukarayannidou, G. Seretoudi, Polymer 38, 16, 4223 (1997)