# Miniemulsion Copolymerization of Ethylene and Vinyl Acetate

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The copolymerizations of a gaseous monomer (ethylene) and a liquid monomer (vinyl acetate) via emulsion and miniemulsion polymerizations are reported. Reactions in which the vinyl acetate was introduced in both batch and semibatch modes are carried out. (Ethylene introduction is always in a semibatch model since the polymerization is carried out under a constant pressure of ethylene in the reactor headspace.) The results are compared, drawing the conclusion that miniemulsion copolymerization has an advantage over conventional emulsion polymerization for monomers with very low water solubility (including gaseous monomers) due to their nucleation in monomer droplets without transport through the aqueous phase.
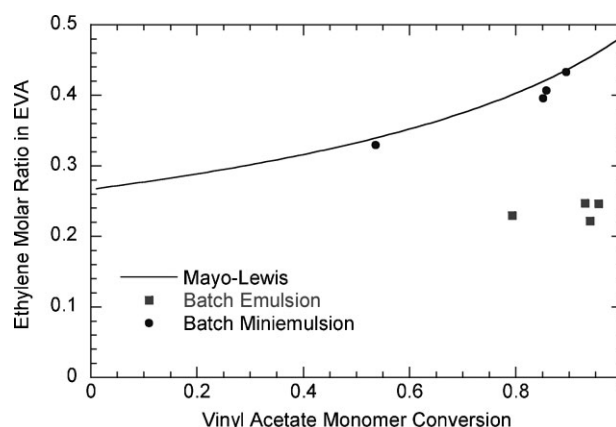
Introduction

Ethylene-vinyl acetate copolymer (EVA) is a commercially important polymer that has been used in a wide range of applications. The properties of EVA copolymer highly depend on the percentage of ethylene in the copolymer. EVA with low ethylene content ranging from 5 to 30 wt.-% is usually produced by the emulsion copolymerization in which ethylene is introduced in a semibatch fashion and functioning as the plasticizer.[1] This type of EVA copolymer is mainly used as adhesive, paint material and coating, or additive in paper manufactory. EVA copolymers with high ethylene content from 60 to 90 wt.-% have good clarity, low-temperature toughness, and resistance to UV radiation. This type of EVA has been used as film material in agricultural industry, packing material in electronic industry, and shock absorber material in sport goods industry. Recently, EVA has been used in the photovoltaic industry as the encapsulation material for the solar photovoltaic modules because of its optical clarity, environmental stability, and low cost.[1] EVA copolymers with high ethylene content are typically produced by bulk or solution copolymerization, which requires high temperature, high pressure, and large amount of solvent. In contrast, emulsion polymerization is a much more moderate process, but the ethylene incorporation is usually limited to less than 30 wt.-% even with high ethylene pressure.[2] The reason is that the ethylene incorporation is governed by the highly limited mass transfer of ethylene from the gas phase to the polymerization loci (polymer particles), since ethylene is highly water insoluble (3.5 mg per 100 mL at 17 °C). In this study, free radical miniemulsion copolymerization of ethylene and vinyl acetate (VAc) is reported. The goal of this study is to investigate the feasibility to enhance the ethylene incorporation using an environmental-friendly miniemulsion polymerization technique.

Emulsion and Miniemulsion Polymerization

Emulsion and miniemulsion polymerizations are significantly different in particle nucleation mechanisms.[3,4]

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A conventional batch emulsion polymerization can be divided into three intervals. Particle nucleation occurs during interval I when majority of the monomers is located in the relatively large (1–10 μm) monomer droplets. Particle nucleation takes place when free radicals formed in the aqueous phase grow via propagation and then enter into micelles or become large enough in the continuous phase to precipitate and form primary particles. Significant nucleation of particles in monomer droplets is discounted because of the small total surface area of the large droplets. Interval II involves polymerization within the monomer-swollen polymer particles with monomer supplied by diffusion from the monomer droplets through the aqueous phase. Interval III begins when the monomer droplets disappear, or at least reach a polymer fraction similar to that of the particles, and continues to the end of the reaction. From the above description, it can be seen that the mass transport from the monomer droplets to the polymerization loci (interval II) can be problematic, if the monomers have very low water solubility.

Previous researches[3,5] suggested that miniemulsion polymerization can provide benefits over the conventional emulsion polymerization in terms of monomer transport. Miniemulsion polymerization involves the use of an effective surfactant/costabilizer system to produce very small (0.01–0.5 μm) monomer droplets.[6] The droplet surface area in miniemulsion system is much larger than those in the conventional emulsion, thus most of the surfactant is adsorbed to the droplet surface, leaving no micelles, and little surfactant to stabilize newly-formed primary particles. Particle nucleation is mainly due to the radical (primary or oligomeric) entry into the monomer droplets (droplet nucleation). The reaction then proceeds by polymerization of the monomer in these small droplets, hence there is no interval II. Monomer transport through the aqueous phase is not relevant in miniemulsion polymerization, thus monomers with very low water solubility (i.e., ethylene) can be effectively incorporated.

As mentioned above, the monomer diffuses from the droplets to the polymerizing particles during interval II in the conventional batch emulsion polymerization. For monomers with favorable water solubility such as VAc (water solubility at 60 °C: 4.3 wt.-%)[7] monomer transport is very rapid, thus the system is reaction, rather than diffusion limited. Even for monomers with as low solubility as styrene (water solubility at 60 °C: 0.24 wt.-%), there is no evidence of transport limitation. However, ethylene has very low water solubility of ≈0.008 wt.-% at 60 °C and 1 atm,[8] which is approximately the same water solubility as vinyl versatate, a monomer known to have very low water solubility.[9] The difference is that vinyl versatate is emulsion copolymerized in small amounts to improve the water resistance of VAc-based coatings, while here we are attempting to include more that 50% (monomer fraction) of

ethylene into VAc. Thus, it is difficult of incorporate large fractions of ethylene into a VA-E copolymer via conventional emulsion copolymerization. This explains the limits of ethylene content of emulsion VA-E as described above. The successful incorporation of other highly water-insoluble monomers via miniemulsion polymerization has been previously demonstrated.[10]

Emulsion copolymerization of ethylene with VAc is commercially practiced.[11–13] Little has been reported on the miniemulsion copolymerization of ethylene in depth. Claverie and coworkers[14,15] and Mecking and coworkers[16–18] have carried out aqueous polymerization of ethylene via catalytic polymerization. Butadiene, another gaseous monomer, has been copolymerized with styrene in miniemulsion.[19,20] The emulsion copolymerization of EVA has been widely studied.[5] Penlidis and coworkers [21–24] have published a model for the emulsion copolymerization of ethylene and VAc. However, there are no reports of free radical miniemulsion polymerization of EVA.

Experimental Part

Materials

Vinyl acetate (VAc 99 + %) was purchased from Aldrich. The inhibitor in VAc was removed by the inhibitor-remover column (from Aldrich) prior to use. Sodium dodecyl sulfate (SDS), potassium persulfate (KPS), hydroquinone, and hexadecane (HD) were all purchased from Aldrich and used as received. High pressure ethylene gas was purchased from Airgas. The water used in this study was de-ionized.

Emulsion and Miniemulsion Preparation

Conventional emulsion copolymerization of ethylene and VAc was performed in this study as the comparison to the miniemulsion copolymerization. The VAc monomer was mixed in the aqueous SDS (surfactant) and KPS (water soluble initiator) solution that was degassed in a vacuum chamber under agitation for 1 h prior to mixing, and the emulsion was created by vigorous agitation. The miniemulsion was prepared by dispersing the VAc–HD (costabilizer) solution into the degassed aqueous SDS–KPS solution to form an emulsion by agitation, and then the emulsion was sheared to make a miniemulsion by sonication using an ultrasonic homogenizer (OmniRuptor 250) for 6 min at 30 W power output. The beaker containing the emulsion was immersed in ice water during the sonication to maintain low temperature.

Experimental Setup

The miniemulsion and emulsion ethylene–VAc copolymerizations were carried out in both batch and semibatch fashions (with respect to the VAc), using the recipe listed in Table 1. The terms batch and semibatch will be taken here to mean with respect to VAc since, by the nature of the process, the ethylene feed is semibatch (fed as needed to keep the ethylene headspace pressure constant,

Table 1. Recipe for EVA emulsion and miniemulsion copolymerization.

	VAc	HD	SDS	KPS	Water	Ethylene
	g	g	g	g	g	kPa
Emulsion	32.0	–	1.0	0.5	160	460
Miniemulsion	32.0	1.6	1.0	0.5	160	460

and hence, the ethylene concentration in the emulsion or miniemulsion approximately constant).

Batch Process

The emulsion or miniemulsion reactant mixture was transferred to a 225 mL high-pressure reaction vessel (Lab-Crest, maximum pressure rating of 720 kPa at 60 °C) equipped with gas inlet and outlet, thermocouple, paddle stirrer, and monomer feed inlet. The system was firstly purged for 10 min using ethylene to remove the air in the headspace of the reactor. After that, the sealed system was

pressurized at 460 kPa with ethylene for 2 h to ensure ethylene saturation in VAc. The reactor was then immersed into an oil bath at 60 °C and the agitation was started. This was defined as the starting point of the copolymerization. The ethylene pressure in the reactor was maintained at 460 kPa. That is to say, ethylene was fed to the reactor whenever the pressure dropped below 460 kPa. The ethylene pressure in the reactor was monitored by an inline pressure transducer, and the ethylene feed flow rate (ethylene polymerization rate) was measured by a mass flow meter. The reaction temperature was also instantly recorded through a thermo-couple. The typical reaction time was 4 h.

Semibatch Process

In semibatch emulsion and miniemulsion copolymerizations, only a portion of total VAc (9.6 g out of 32 g) was initially used to prepare the emulsion or miniemulsion and subsequently transferred into the reactor. The procedures prior to the start of polymerization were as same as these in the batch reactions. When the reaction was started, the rest for the VAc monomer (22.4 g out of 32 g) was simultaneously fed into the reactor using a high pressure pump through the feed inlet. Three feeding rates were used, namely 0.1, 0.2, and 0.3 mL · min^{-1}, resulting in 240, 120, and 80 min feeding intervals, respectively. The VAc feed was dropped at the center of the agitation, and the feed inlet was closed immediately after the feeding was finished. The pressure in the reactor was maintained at 460 kPa and the total reaction time was kept as 4 h.

Analytical Techniques

The gravimetric method was used to determine the conversion of VAc and the composition of the final EVA copolymer. A small amount of the latex sample was taken from the reactor after the polymerization was terminated by adding a few drops of 5 wt.-% hydroquinone water solution and the reactor was immersed into ice water. The latex sample (wet sample) was weighed and then dried at 50 °C for 24 h in a vacuum oven. After drying, the weight of the sample (dry sample) was measured again. Samples consisted of the follows components:

Wet Sample

$$= PVAc + VAc + SDS + KPS + Water + Et + HD$$

$$Dry\ Sample = PVAc + SDS + KPS + Et$$

Given the reactor headspace volume, the ethylene consumption during the copolymerization can be calculated as a function of time from the instantaneous ethylene pressure, flow rate, and temperature data. With the ethylene consumption, the VAc monomer conversion can be determined using the following format:

$$VAc\ Conversion = \frac{Dried\ Sample\text{-}Ethylene\text{-}(Wet\ Sample\text{-}Ethylene) \times (SDS + KPS)wt.\text{-}\%\ in\ Recipe}{(Wet\ Sample\text{-}Ethylene) \times VAc\ wt.\text{-}\%\ in\ Recipe}$$

EVA copolymer composition was also determined using proton nuclear magnetic resonance spectroscopy (^{1}H NMR) using CDCl$_3$ as the solvent. The molecular weight and the molecular weight distribution were measured by gel permeation chromatography (GPC) with a Waters 410 differential refractometer operated at 30 °C. HPLC grade chloroform was used as the solvent carrier (0.6 mL · min^{-1}). Five polystyrene standards with molecular weight of 575 000, 200 700, 90 000, 9 500, and 2 000, respectively, were used in the GPC test. For the ^{1}H NMR and GPC tests, no gel formation was observed during the sample preparation, i.e., the EVA samples were completely dissolved in the CDCl$_3$ and chloroform, respectively. The glass transition temperatures of the EVA copolymers were measured by thermal analysis with a differential scanning calorimeter (DSC, TA Instruments Q100). A heat-cool-heat cycle was applied from −60 to 80 °C. The heating rate was 10 °C · min^{-1} and the cooling rate was 5 °C · min^{-1}.

Results and Discussion

Batch EVA Emulsion and Miniemulsion Copolymerization

The EVA copolymer composition was obtained using ^{1}H NMR as Figure 1 showing a representative spectrum. In Figure 1, the peak at 4.85 ppm corresponds to the α-H (CH in VAc segment); the broad peak from 1.55 to 1.83 ppm represents the β-H (CH$_2$ in VAc segment); the CH$_3$ group of VAc appears as a peak at 2.0 ppm. The CH$_2$ peak of ethylene segment appears at 1.23 ppm. The peak at 0.86 ppm
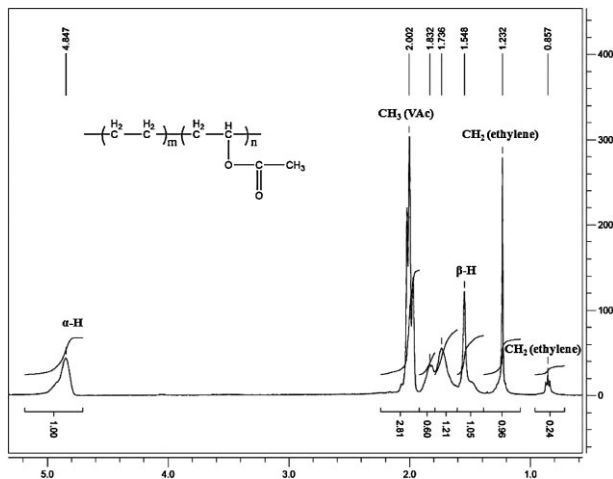
Figure 1. ^{1}H NMR spectrum of EVA copolymer.

corresponds to the CH_3 group derived from H-abstraction by the ethylene CH_2 radical. The molar ratio of ethylene to VAc in the EVA copolymer was calculated using the following equation:

$$E : VAc = \frac{I_{0.8-2.3ppm} - 5I_{4.9ppm}}{4I_{4.9ppm}} \qquad (1)$$

where I represents the integral of a peak in the ^{1}H NMR spectra.

EVA compositions obtained with both ^{1}H NMR and gravimetric analyses are listed in Table 2 for comparison. It can be seen that the results from these two methods are in good agreement.

The composition of EVA copolymer from the bulk batch copolymerization can be calculated as a function of VAc

Table 2. Ethylene content in EVA—batch reaction.

Sample code	Ethylene molar ratio in EVA	
	Gravimetric	^{1}H NMR
Batch emulsion		
EVAe1[a]	0.230	0.227
EVAe2	0.246	0.230
EVAe3	0.222	0.256
EVAe4	0.247	0.216
Batch miniemulsion		
EVAm1[a]	0.333	0.326
EVAm2	0.433	0.418
EVAm3	0.407	0.382
EVAm4	0.396	0.356

[a]Reaction time is 3 h.

conversion using the Mayo–Lewis equation:

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \qquad (2)$$

where F_1 is the instantaneous mole fraction of ethylene in EVA copolymer being formed, f_1 the instantaneous mole fraction of ethylene in the monomer mixture, and f_2 is the instantaneous mole fraction of VAc in the monomer mixture; r_1 and r_2 are the reactivity ratios for ethylene and VAc, respectively. In order to obtain the instantaneous monomer fraction, the solubility of ethylene in VAc under the experimental condition was measured using the same procedure described in the Experimental Part, replacing the reactant mixture with pure VAc. From the reactor pressure, temperature, and ethylene flow rate data, given the headspace volume, the amount of ethylene dissolved in VAc was calculated. The solubility experiments were done in triplicate, and the averaged solubility of ethylene in VAc under the experimental condition was $0.362 \pm 0.029\,mol_{ethylene}/mol_{VAc}$. Since the ethylene pressure was kept at 460 kPa throughout the polymerization, we assume the VAc was always saturated with ethylene. Thus, f_1, the instantaneous mole fraction of ethylene in the monomer mixture, was a constant that could be calculated based on the solubility of ethylene in VAc. The instantaneous mole fraction of VAc in the monomer mixture, f_2 can be calculated based on f_1 as a function of VAc conversion. For high pressure bulk copolymerization of ethylene and VAc, the reactivity ratios of ethylene and VAc are both unity.[25,26] Therefore, the EVA copolymer composition in bulk copolymerization was calculated using the Mayo–Lewis equation as a function of VAc conversion.

Figure 2 shows the calculated Mayo–Lewis curve for bulk copolymerization of ethylene and VAc alongside the
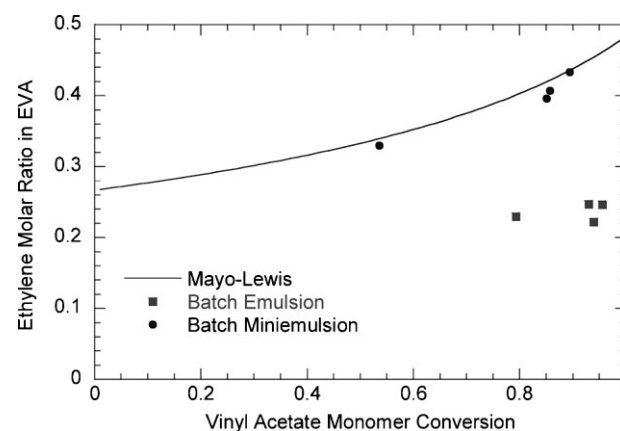

Figure 2. Ethylene content in EVA from batch emulsion and miniemulsion polymerization as a function of vinyl acetate conversion.

experimental results from both emulsion and miniemulsion batch copolymerizations. It can be seen that the miniemulsion results are in very good agreement with the ideal bulk copolymerization curve, which the emulsion polymerization results are obviously below. At similar VAc conversion, EVA copolymer from the miniemulsion contains substantially higher ethylene content. This observation clearly suggests that the miniemulsion copolymerization of ethylene and VAc is superior to conventional unseeded emulsion copolymerization. In the emulsion polymerization, ethylene is trapped in the large monomer droplets of ethylene–VAc from which it has to diffuse through the water phase to the locus of polymerization. This is significant for monomers with low water solubility such as ethylene. In contrast, the miniemulsion polymerization does not involve ethylene diffusion across the water phase from large monomer droplets to polymerization loci, since the polymerization takes place in the monomer droplets. It must be noted, however, that the diffusion of the ethylene feed through the aqueous phase into the forming EVA particles must take place in both emulsion and miniemulsion polymerization. In EVA miniemulsion copolymerization, each droplet containing VAc and ethylene monomers can be considered as an individual reactor. In such a reactor, the copolymerization can be considered as bulk polymerization with constant ethylene concentration because of the ethylene feeding at constant pressure, which could be the reason that the composition of EVA from miniemulsion is so close to that from the bulk copolymerization. In summary, Figure 2 is a strong evidence to prove that conventional emulsion polymerization is mass transfer limited, and miniemulsion polymerization can overcome this obstacle.

The EVA copolymers were also characterized using DSC to obtain their glass transition temperatures (T_g) as shown in Figure 3. The EVA copolymer from emulsion batch copolymerization showed single glass transition around
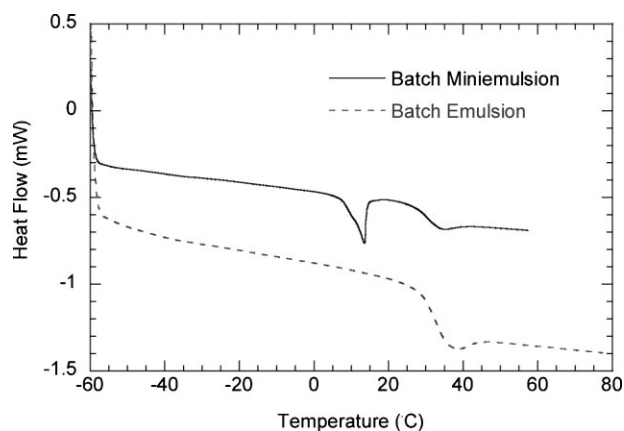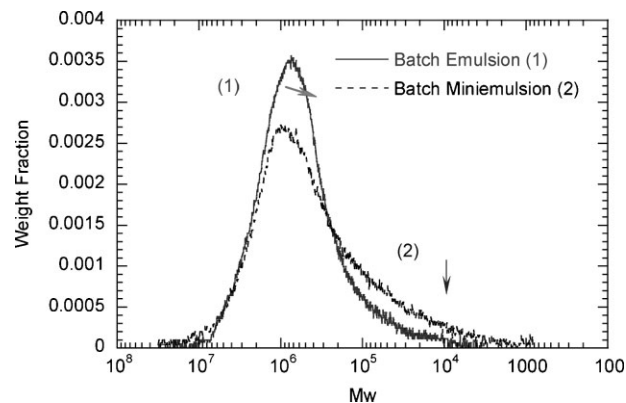

Figure 4. Molecular weight distribution of EVA copolymers via batch emulsion and miniemulsion copolymerizations.

26 °C, and the EVA copolymer from miniemulsion showed glass transition around 35 °C. It was noticed that the miniemulsion sample shows an endothermic peak on the heating circle. It is due to the HD residue that has a melting point of 18 °C.

The representative molecular weight distributions of the EVA copolymers are shown in Figure 4. EVA copolymers from batch emulsion and miniemulsion copolymerizations have similar weight average molecular weight between 800 000 and 900 000 g·mol^{-1}. The molecular weight distribution from miniemulsion (polydispersity = 4.4) is slightly broader than that from emulsion (polydispersity = 3.5). This may have been caused by some fraction of homogenous nucleation in the aqueous phase in the miniemulsion copolymerization, since VAc monomer has relatively high solubility (4.3 wt.-% at 60 °C) in water. VAc miniemulsion is known to exhibit small amount of homogeneous nucleation.[27]

Semibatch EVA Emulsion and Miniemulsion Copolymerizations

The composition of EVA copolymers from semibatch emulsion and miniemulsion copolymerizations were also analyzed by the gravimetric method and ^{1}H NMR spectra. The results are listed in Table 3, from which it can be seen that the results from these two methods are in good agreement.

These experimental results are added on Figure 2 to compare to the data from batch copolymerizations as shown in Figure 5. It can be seen that the ethylene content in the EVA copolymers from semibatch are much higher than the ones from batch copolymerizations. The VAc conversion is higher and the ethylene content is lower with increased VAc feeding rate for semibatch copolymerizations. This is because that the VAc feed can more easily transport to the polymerization loci than ethylene does, the instantaneous ethylene/VAc ratio is lower at higher VAc

Figure 3. DSC of EVA copolymers via batch emulsion and miniemulsion copolymerizations.

Table 3. Ethylene Content in EVA—semibatch reaction.

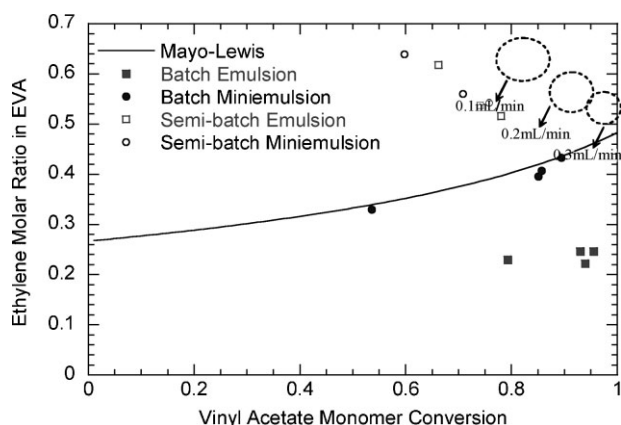| Sample code (ethylene feed rate)	Ethylene molar ratio in EVA	
	Gravimetric	^{1}H NMR
Semibatch emulsion		
EVAse1 (0.1 mL · min^{-1})	0.618	0.651
EVAse2 (0.2 mL · min^{-1})	0.537	0.578
EVAse3 (0.3 mL · min^{-1})	0.516	0.519
Semibatch miniemulsion		
EVAsm1 (0.1 mL · min^{-1})	0.639	0.661
EVAsm2 (0.2 mL · min^{-1})	0.59	0.600
EVAsm3 (0.3 mL · min^{-1})	0.542	0.558

Figure 5. Ethylene content in EVA as function of vinyl acetate conversion.

feeding rate. It also can be seen that at the same VAc feeding rate, the EVA copolymers from semibatch miniemulsions always have lower VAc conversion and higher ethylene composition than those from semibatch emulsions. This difference originated from the different seeding conditions of the semibatch emulsion and miniemulsion copolymerizations: 9.6 g VAc saturated with ethylene was initially charged into the reactor as emulsion and miniemulsion, respectively. After the polymerization started in the emulsion, the transport of ethylene dissolved in this part of VAc was constrained. Therefore, despite the ethylene feed has to diffuse through the water phase to the polymerization loci in both emulsion and miniemulsion, ethylene incorporation in miniemulsion is slightly better because of the monomer droplet nucleation mechanism. If the semibatch reactions were run under monomer (VAc) starved conditions, it is likely that the difference in ethylene incorporation between the emulsion and miniemulsion would be eliminated.
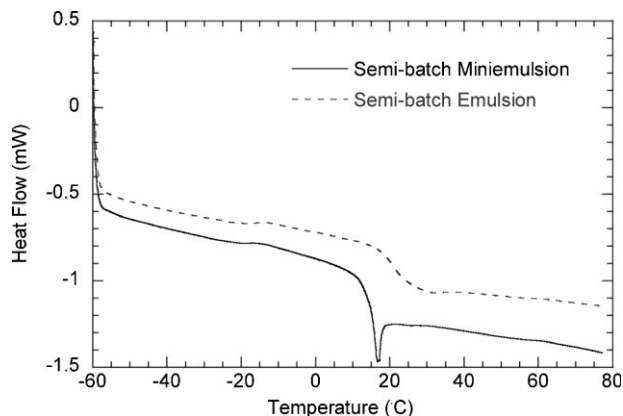

Figure 6. DSC of EVA copolymers via semibatch emulsion and miniemulsion copolymerization.

The DSC analysis (Figure 6) shows that the EVA copolymers from the semibatch have lower T_g ($\sim$20 °C) than the ones from batch reaction, which is consistent with the higher ethylene incorporation. The EVA copolymers from emulsion and miniemulsion semibatch have almost identical molecular weight OF about 900 000 g · mol^{-1} (Figure 7). The molecular weight distributions are similar and are broader than the ones from batch process, as would be expected.

Conclusion

This preliminary study has demonstrated that conventional batch emulsion copolymerization of ethylene and VAc is controlled by the monomer transfer from the droplets to the polymerization locus through the aqueous phase, which greatly limits the incorporation of water
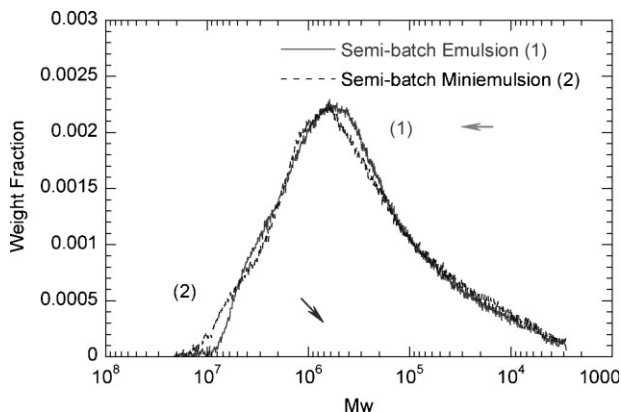

Figure 7. Molecular weight distribution of EVA copolymers via semibatch emulsion and miniemulsion copolymerization.

insoluble ethylene. In contrast, batch miniemulsion copolymerization can overcome this problem because of its unique droplet nucleation mechanism. Miniemulsion batch copolymerization allows higher ethylene incorporation. When semibatch processes are used, the miniemulsion system results in higher ethylene incorporation than the emulsion system, but the effect is much diminished. It is likely that if the semibatch systems were run under VAc-starved conditions, the advantage of the miniemulsion system would disappear completely.

Miniemulsion copolymerization of ethylene and VAc can potentially lead to the high ethylene content EVA copolymer via an economic and environmental-friendly process. Future work will include detailed kinetics study and the effects of surfactant concentration, types of initiator and ethylene pressure. The nucleation mechanism in semibatch miniemulsion polymerization will also be studied.

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