Dispersion Polymerization of Methyl Methacrylate with Hydrocarbon Surfmers and Long Chain Fatty Acids as Dispersion Reagents.

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ABSTRACT: Vinyl monomers that consist of carbonyl group and –OH group are found to be act as surfmers (surfactant + monomer) in the polymerization process that uses supercritical CO_2 ($scCO_2$) as a solvent. By co-polymerization of methyl methacrylate (MMA) with methacrylic acid (MAA) and acrylic acid (AA) in $scCO_2$, micropowder of poly(MMA) (pMMA) was successfully obtained. The polymerization mechanism was examined with the MMA/MAA systems. From the experiments, it was revealed that the addition of surfmer MAA forms dispersion phase in the $scCO_2$ that enables the dispersion polymerization of MMA without fluorinated surfactants.

As a natural consideration of the above results, effects of long chain fatty acids and poly(methacrylic acid) were examined with MMA. It was found that these compounds also act as dispersion reagents in the $scCO_2$, and successfully formed MMA micropowder. In the course of the investigation, it was also found that changing the chain length of the fatty acids gave a very interesting crystal shaped polymer particles without any special operations.

I. INTRODUCTION

Recently, global scale environmental damage such as warming, ozone layer depletion, and acid rain becomes large problem. Therefore, the severe pollution control had begun to carried out in many countries worldwide, and the conversion of conventional industrial process to more environmentally friendly process have been required. Volatile organic solvents (VOS) are one of the causes of the photochemical smog with the hydrocarbons that are included in the automotive exhaust gas of the automobile. The regulation for the effluent of VOS will become more severe in the near future.

As an alternative to the VOS, many researchers are looking forward to supercritical carbon dioxide ($scCO_2$). $ScCO_2$ is non-toxic, inflammable, and environmentally benign fluid. One of the most promising industrial processes for the utilization of $scCO_2$ is a polymerization process. As the CO_2 is chemically stable, it is inert for radicals, and need no drying process because it is a gas under the ambient condition. Unfortunately, $scCO_2$ does not dissolves most polymers except for high pressures and temperatures [1]. To utilize the SC-CO_2 as an alternative solvent in the polymerization process, effective surfactant must be developed to overcome this low solubility. In the present stage of the study, only polymers which contain perfluoroalkyl side chains, or their block copolymers are the most effective surfactant for dispersion polymerization [2]. Unfortunately, compounds those consist perfluoroalkyl group are expensive.

In our previous study [3-6], it was found vinyl monomers those have carboxyl acid such as acrylic acid and methacrylic acid work as surfmers (surfactant + monomer). In this study, the effects of these surfmers were thoroughly examined. At the same time, on the postulate that if the carboxyl acid works as surfactant, aliphatic carboxyl acids will have surfactant like natures in $scCO_2$, effects of aliphatic carboxyl acids on the radical polymerization of MMA in $scCO_2$ were also examined.

Figure 1. Schematic representation of the polymerization apparatus.

II. EXPERIMENTAL

(1) MATERIALS: Methyl Methacrylate (MMA) was purchased from Wako Pure Chemical Co. Ltd., and used as a main monomer. Before use, MMA was washed first by 20wt% NaOH and then 20wt% Nacl aqueous solutions for three times, and then dried with $CaCl_2$ for 1 night. It was then distilled under reduced pressure, and stored in refrigerator. Acrylic acid (AA) and methacrylic acid (MAA) were used as surfmers without further treatment. For the initiator, AIBN was used. AIBN was recrystallized twice from hot methanol. Five aliphatic carboxyl acids, Enathic Acid, Myristic Acid, Docosanoic Acid, Dodecanedioic Acid, and 2-n-Hexa-decylstearic were used as dispersion reagent. All of the reagents were purchased from Wako Pure Chemicals Co. Ltd., and used as received. Carbon dioxide (CO_2) was used as a solvent after dehydration and deoxidization.

(2) APPARATUS and PROCEDURE: **Figure 1** shows schematic figure of batch type polymerization apparatus. Volume of the polymerization cell is c.a. $50cm^3$. In general, monomer (1 mol/L) and AIBN ($2.61x10^{-3}$ mol/L) are mixed in the polymerization cell, and pressurized to the

Figure 2. Schematic representation of view cell type polymerization apparatus.
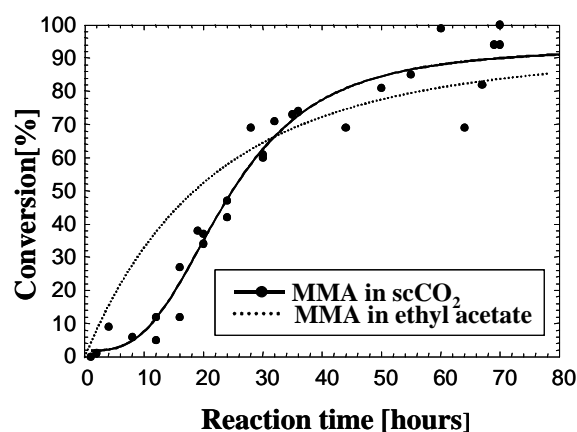
Figure 3. Conversion of homo-polymerization of MMA in $scCO_2$.

experimental condition. Polymerization is conducted at 65°C and 30MPa. Conversion of the monomer is calculated by the weight of polymer remained in the polymerization cell after the depressurization. **Figure 2** shows view type polymerization apparatus to see the phase condition during the polymerization. Setup of the apparatus is almost the same with the batch type apparatus shown in Figure 1 except for the view cell.
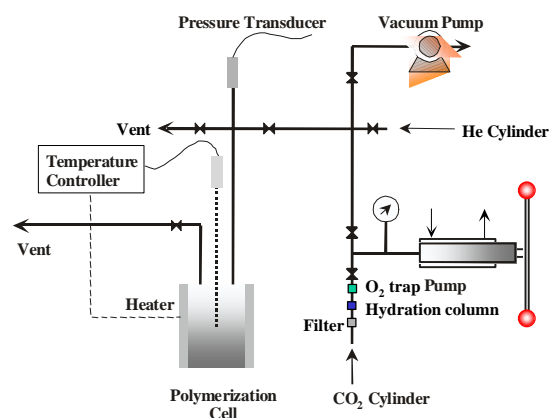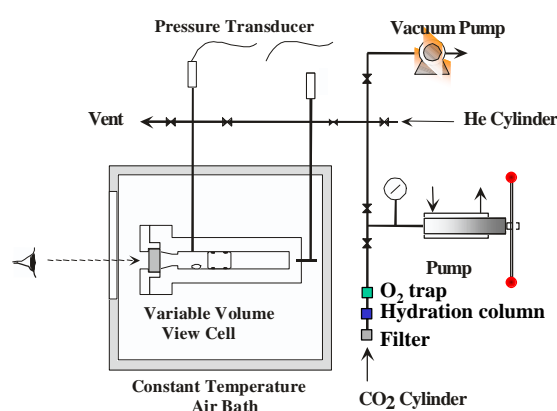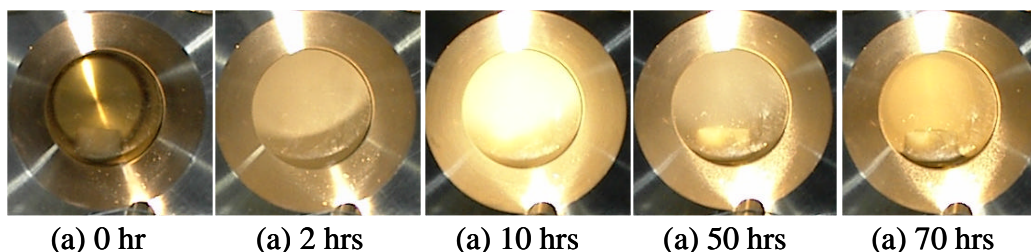
(a) 0 hr　　　(a) 2 hrs　　　(a) 10 hrs　　　(a) 50 hrs　　　(a) 70 hrs

Figure 4. Photographs of the phase in the view cell during the polymerization of MMA.

III. RESULTS AND DISCUSSION

Figure 3 shows conversion of the homo polymerization of MMA in $scCO_2$. Conversion of MMA in ethyl acetate (EA) is also shown for comparison. At first, polymerization rate is lower than that in the EA, but accelerate after 10-20 hours. **Figure 4** shows appearance of the solution during the polymerization. Visual observation clearly revealed the clear mixture of MMA, AIBN and $scCO_2$ becomes turbid after 2 hrs, and begun to form precipitate phase after 10 hrs, at which the acceleration of polymerization occurs. Thus, the acceleration is probably due to the gel effect caused by the precipitation of MMA during the polymerization.

Figure 5 shows molecular weight of poly(MMA) (pMMA) measured by a GPC. Average molecular weight, unlike the radical polymerization, increased with time during the polymerization. As the GPC chart showed clear three peaks, peak separation was performed, and shown in Figure 5. The results suggest the existence of three different location of polymerization. They are probably (1) $scCO_2$ phase for radicals just after the cleavage (peak 1), (2) dispersed pMMA oligomer phase in $scCO_2$ (Peak 2), and (3) precipitate pMMA bulk phase (peak 3) in which the gel effect will occur. As the polymerization proceeds, the amount of precipitate phase increases to cause a acceleration of reaction rate due to the gel effects.
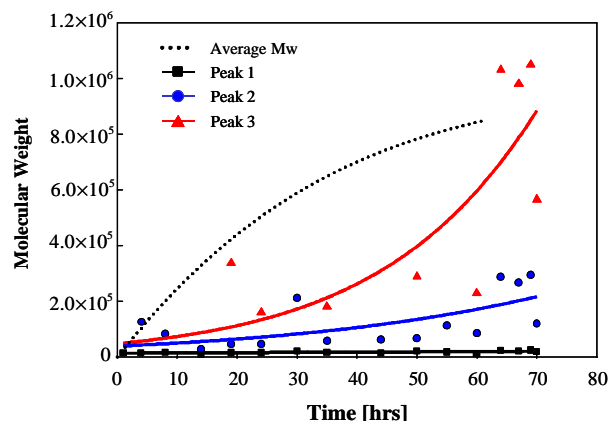

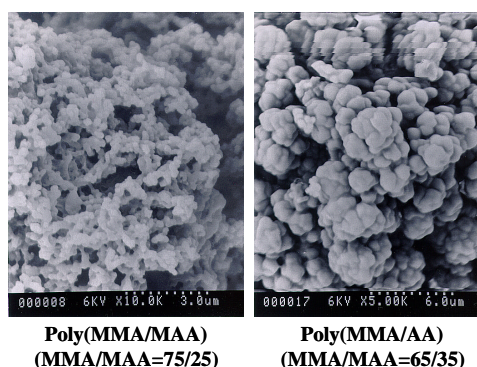
Figure 5. Molecular weight of pMMA.

Poly(MMA/MAA)　　　Poly(MMA/AA)
(MMA/MAA=75/25)　　(MMA/MAA=65/35)

Figure 6. SEM images of products of MMA/MAA and MMA/AA systems.
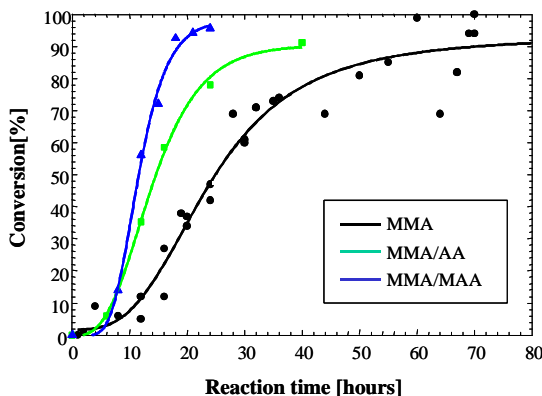
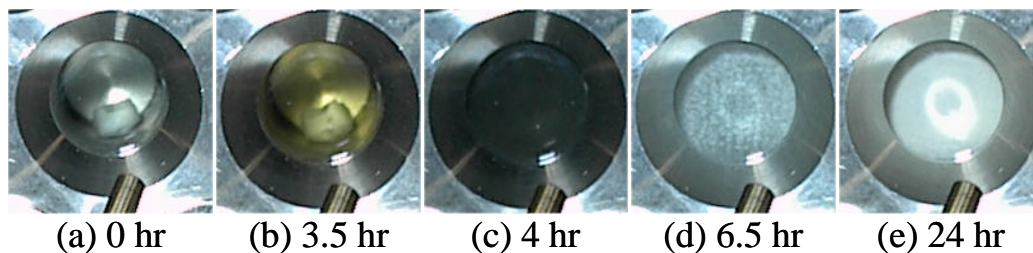**Figure 7. Conversion of monomers for MMA, MMA/AA, and MMA/MAA systems.**

(a) 0 hr   (b) 3.5 hr   (c) 4 hr   (d) 6.5 hr   (e) 24 hr

Figure 8. Photographs of the phase in the view cell during the polymerization of MMA/AA. The molar ratio of monomers were 65/35.

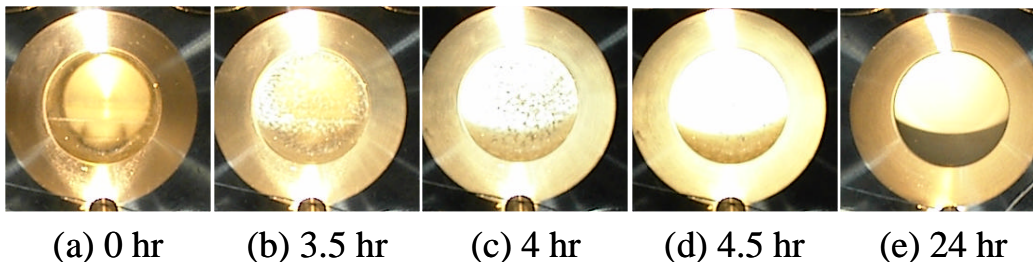(a) 0 hr   (b) 3.5 hr   (c) 4 hr   (d) 4.5 hr   (e) 24 hr

Figure 9. Photographs of the phase in the view cell during the polymerization of MMA/MAA. The molar ratio of monomers were 90/10.

Co-polymerization of MMA with MAA or AA gave fine white polymer powder that has slight static charge. **Figure 6** shows SEM images of the polymer powder. It could be seen from the figure that the particle consisted of small primary particles. **Figure 7** shows the conversion of monomers with surfmers. The molar composition of monomers were MMA/MAA=90/10 and MMA/AA=65/35. The reaction rate accelerated significantly with the co-polymerization of surfmers. **Figures 8 and 9** show the appearance of the solution during the polymerization. Compared with the Figure 4, it reveals that the dispersed state formed at the initial stage holds to the end of the polymerization. Further, the dispersion ability of the MAA was greater than AA. GPC charts of the products have only one peak, and the average molecular weight was independent of the polymerization time to be 2.4×10^5. Further, the thermal analysis of the products showed only one Tg peak between MMA and MAA or AA, which means molecular mixing of the monomers. From above facts, the mechanism of the co-polymerization was assumed as follows: At fires, monomers and oligomers form uniform mixture due to the co-solvent effects of monomers. As the polymerization proceeds, molecular weight of oligomer increases to form dispersion phase. Once formed dispersion phase does not coagulate because of the repulsion of –OH groups. Subsequent polymerization proceeds mainly in the dispersed phase that causes gel effects to accelerate reaction rate.

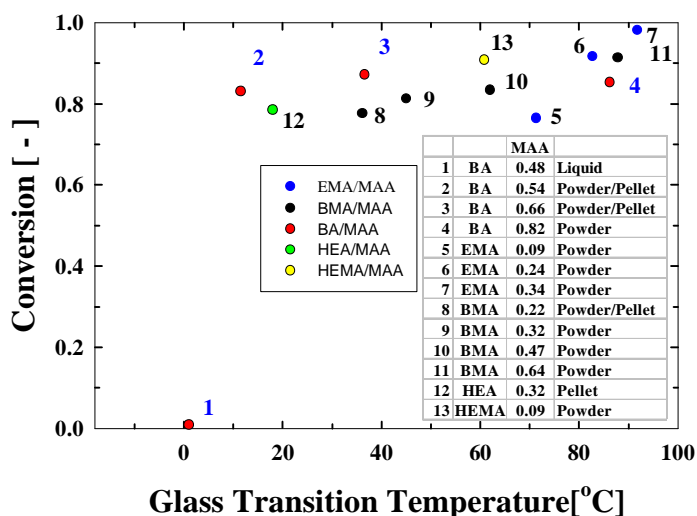In the previous work, we pointed out that polymers that have Tg lower than 60 $^{\circ}$C can not

		MAA	
1	BA	0.48	Liquid
2	BA	0.54	Powder/Pellet
3	BA	0.66	Powder/Pellet
4	BA	0.82	Powder
5	EMA	0.09	Powder
6	EMA	0.24	Powder
7	EMA	0.34	Powder
8	BMA	0.22	Powder/Pellet
9	BMA	0.32	Powder
10	BMA	0.47	Powder
11	BMA	0.64	Powder
12	HEA	0.32	Pellet
13	HEMA	0.09	Powder

Figure 10. Relationship between Tg and initial monomer composition.

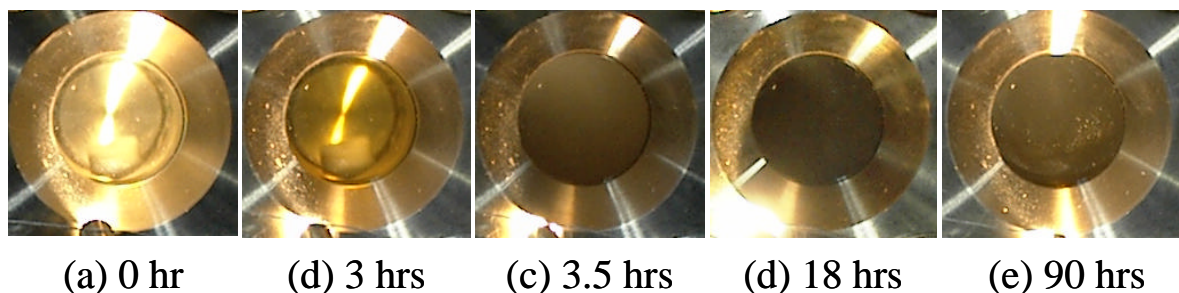(a) 0 hr   (d) 3 hrs   (c) 3.5 hrs   (d) 18 hrs   (e) 90 hrs

Figure 11. Photographs of the phase in the view cell during the polymerization of MMA/Myristic Acid. The molar ratio of monomers were 84/16.

polymerized even with the fluorinated surfactants due to their easiness to coagulate [3,4]. With using the MMA and AA as surfmers, we examined the polymerization of low Tg polymers such as butyl acrylate and ethyl methacrylate. **Figure 10** shows that the addition of surfmers makes it possible to polymerize low Tg polymers.

For the natural extension of above results, we examined the effects of aliphatic carboxyl acid as surfactants. **Figure 11** shows appearance of the solution during the polymerization of MMA/myristic acid for example. It is clear that the addition of myristic acid stabilizes the dispersion to the end of the polymerization. **Figure 12** sows effects of aliphatic carboxylic acids on the conversion of MMA. As could be seen from the figure, longer the hydrocarbon chain, greater the dispersion ability. Further, dodecanedioic acid that has two carboxylic acid groups exhibited stronger ability than docosanoic acid that has one carboxylic acid group. Cleary, the carboxylic acid group acts as a surfactant in the polymerization of MMA in $scCO_2$. The extent of the surface activity could be found in our report [8].

At the same time, there are tendency that the polymerization products with aliphatic carboxylic acids has spherical structure with increasing carbon chain length. **Figure 13** shows SEM images of pMMA obtained with different aliphatic carboxylic acids. It is very interesting that with the myristic acid, glistering powder
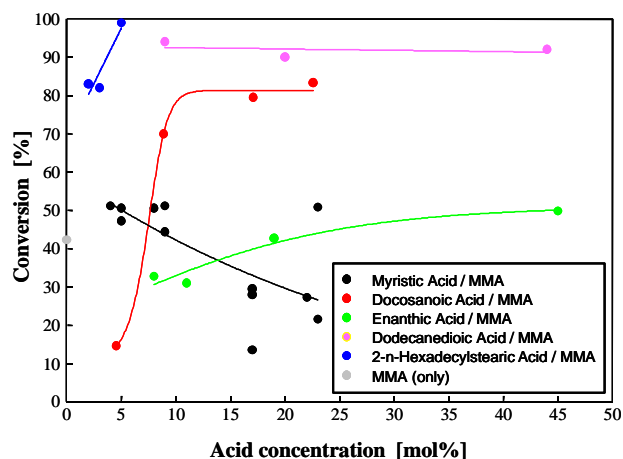

Figure 12. Effects of aliphatic carboxyl acids on the conversion of MMA.
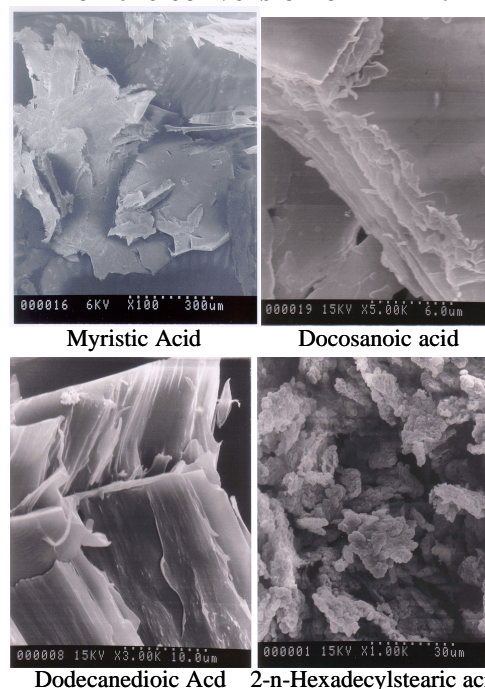

Myristic Acid   Docosanoic acid

Dodecanedioic Acd   2-n-Hexadecylstearic acid

Figure 13. SEM images of pMMA particle obtained with aliphatic carboxylic acids.

that has lamellar like structure was obtained. Clearly, aliphatic carboxylic acids forms self aggregate structure in the polymerization medium.

The effects of poly methacrylic acid (pMAA) was also examined. **Figure 14** shows the effects of pMMA on the conversion of MMA. Conversion of butyl methacrylate (BMA) / MAA systems are also shown for comparison. Figure 15 shows SEM image of the product of BMA/pMAA system. PMAA has a greater ability than MAA for the formation of polyBMA powders. Visual observation of polymerization revealed that the polymerization occurred in the swollen pMAA phase.

Figure 14. Effects on PMAA on the conversion of MMA. (BMA/pMAA=94/6)

IV. CONCLUSION

In this study, both vinyl carboxylic acids and aliphatic carboxylic acids were shown to possess a surface activity for the polymerization in scCO$_2$. It is presumably due to the static repulsion of –OH groups. At the same time, the pMAA was also shown to behave as macrosurfactant for the polymerization.

It has bees said that the fluorinated polymeric surfactants are necessary for the dispersion polymerization in scCO$_2$. We believe that our result opens vast possibility of constructing an economically acceptable and simple process for the polymerization with scCO$_2$ as solvent.

Figure 15. SEM image of BMA/pMAA product.

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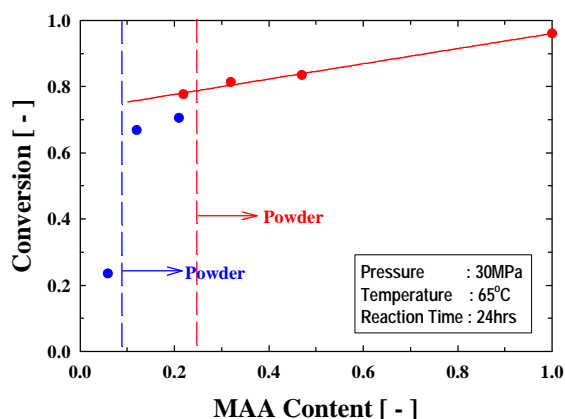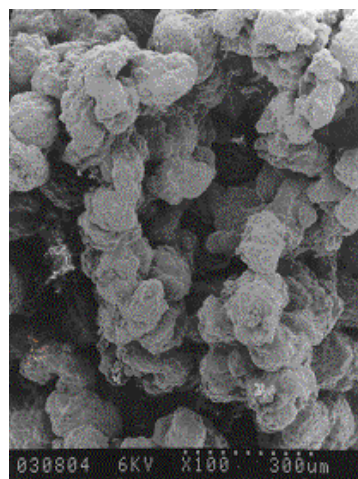[7] Ellis, M. F.; Taylor, T. W.; Jensen, K. F. AIChE J., Vol.40, **1994**, p.445