Preparation and Characterization of Acrylic Polymers Based on a Novel Acrylic Monomer Produced from Vegetable Oil

Hang-Goo Cho,[1,2] Seong-Yung Park,[1] Jonggeon Jegal,[1] Bong-Keun Song,[1] Hyung-Joong Kim[2]

[1]*Industrial Biochemical Research Center, Korea Research Institute of Chemical Technology, Yusung, Daejon 305-600, Korea*
[2]*Department of Advanced Material Engineering, Kongju National University, Kongju, Chungnam 314-701, Korea*

Received 7 October 2008; accepted 26 August 2009
DOI 10.1002/app.31467
Published online 10 December 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: To prepare polymers based on the vegetable oils, an acrylic monomer with long alkyl chain, (2-(acryloyloxy) ethyl oleate) (AEO)), was prepared by the reaction of hydroxyl ethyl acrylate (HEA) with methyl oleate (MO), in which the MO, having very similar structure to the bio-diesel, was the one derived from Linseed oil. For the formation of the AEO, Novozyme-435, the *Candida antarctica* lipase B loaded on the acrylic resin, was used as a catalyst. To optimize its reaction condition, effects of experimental factors, such as, different enzymes, reaction temperature, water activity of enzyme, concentration of enzyme used, and molar ratio of HEA and MO, were studied. The AEO was then, after characterization using several analytical methods, polymerized by the radical polymerization, using benzoyl peroxide (BPO) as a catalyst. The M_n of the polymers prepared under different experimental conditions was in the range from 20,000 to 30,000 g/mol. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 736–742, 2010

Key words: polyacrylate; vegetable oil; acrylic monomer; methyl oleate

INTRODUCTION

With deteriorating environment, recently, environmental friendly materials have been attracting more attention.[1] One of the phenomena about this is the appearance of the bio-based polymers, so called Bioplastics, in the plastic market. With CO_2 neutralization concept, most of the bioplastics based on the biomass is known not to produce surplus CO_2, and they are also biodegradable. Because of such characteristics of the bioplastics, it is becoming mega-trend in the polymer technology to produce useful new polymers from bio-mass. Another thing currently being considered is the environmental friendly reaction, not to use toxic chemicals. The toxic chemical catalyst that has long been widely used for the synthesis of organic polymers needs to be replaced by more safe bio-catalysts, such as, enzymes.

When compared with the classical chemical reaction, enzymatic synthesis, such as, enzymatic polymerization, using different kinds of enzymes is considered as a much more safe process due to the characteristics of enzymes. Among the advantages of the enzymatic reactions are mild reaction conditions not using high temperature and high pressure, and highly selective reactions for instance to produce chiral active materials. Also enzymatic reaction is region-specific that unwanted side reaction can be avoided.[2–4] Lipases, for example, such as Novozyme 435 derived from *Candida actarctica* (Denmark), CAL-B (lipase immobilized, Genofocus), have been known to be effective for esterification and transesterification under organic solvent condition with trace amount of water.[5,6] Recently, such enzymes have been used for the formation of biodiesel from plant oils through the transesterification.[7–15] Exploring the possibility of the enzymes for several organic reactions, such as, esterification, transesterification, hydrolysis, acoholysis, and aminolysis, enzymes are more often used for the organic reaction.[16–22]

In this study, (2-(acryloyloxy) ethyl oleate) (AEO)) was synthesized to encourage the use of methyl oleate (MO) derived from Linseed oil for the polymerization of bio-based polymers. The AEO was also produced by the environmental friendly enzymatic reaction using Novozyme-435 (derived from *Candida actarctica*, Denmark) as a bio-catalyst. During the synthesis of AEO, effects of the different kinds of lipases, reaction temperature, water activity (a_w) on the conversion ratio with reaction time were studied.[23] After characterization of AEO using instrument analytical methods, it was polymerized by the radical polymerization using benzoyl peroxide

Correspondence to: J. Jegal (jggegal@krict.re.kr).

(BPO) as an initiator and its polymerization conditions were studied, changing several experimental factors, such as, concentration of initiator and concentration of monomer. The details are as follows.

EXPERIMENTAL

Materials

Hydroxy ethyl acrylate (HEA, 97%) and MO (99%) purchased from Aldrich Chemical Co. were used without further purification. Novozyme-435 (derived from *Candida actarctica*, Denmark), CAL-B (lipase immobilized, Genofocus), Lipozyme RM IM (Lipo RM IM, Novozymes), Lipozyme TL IM (Lipo TL IM, Novozymes) were used as a bio-catalyst. Toluene (HPLC grade, Aldrich, 99.9%) was used as solvent after removal of water using KOH. Molecular Sieve [5 Å purchased from Acros (bead form, MS)] was also used for the acceleration of the reaction. Hydroquinone (HQ, 99%, purchased from Aldrich) was used without further purification as radical scavenger. BPO (75%, purchased from Aldrich) was used after recrystallization from methanol as a radical initiator. Methylmethacrylate (MMA, 99.9%, purchased from Aldrich) and styrene (St, 99.0%, purchased from Wako) was used as monomer without purification. For the crosslinking of the acrylic polymer, 2-butanone peroxide (MEKPO, ca. 35 wt %, solution in 2,2,4-trimethyl-1,3-pentanediol diisobutylate, purchased from Aldrich) and cobalt naphthalene (Co-Nap, purchased from Wako pure chemical) were used as an initiator and a crosslinking accelerating agent, respectively.

Synthesis of an acrylic monomer

The acryl monomer, 2-(acryloyloxy) ethyl oleate (AEO), was synthesized by the transesterification of HEA with MO: 5.806 g (0.05 mol) of HEA and 5.930 g (0.02 mol) of MO dissolved in 24 mL of toluene were reacted under nitrogen at 50°C for 24 h with the aid of 1.2 g (10% of monomers) of Novozyme 435 as a catalyst. The reaction solution contained 1.5 g of molecular sieve with its pore size of 5 Å for the removal of methanol being produced during the reaction. The toluene and HEA were completely dried by the vacuum distillation before use. After completion of the reaction, the product was purified as follows; first, the reaction solution was vacuum dried at room temperature to remove toluene, and then the product obtained was dissolved into 30 mL of hexane again and filtered using a filter paper to remove the Novozyme 435 used as catalyst out of the solution. After that, to completely remove the HEA remained in the solution, the hexane solution was washed for several times with the mixture solution of acetonitrile and deionized water (1 : 1 in volume ratio) using a separation column. The hexane solution was then vacuum-distilled to remove the solvent hexane and to obtain the monomer.

Homopolymerization of AEO

The AEO prepared was polymerized by the bulk polymerization using BPO as an initiator: 5.0 g of AEO and 0.5 g of BPO were added into 20 mL round-bottom flask and polymerized under nitrogen at 80°C for 24 h with constant stirring with a mechanical stirrer. After completion of the polymerization, the copolymers were purified by the precipitation method in the nonsolvent, such as, ethanol.

Copolymerization with MMA

To prepare a coating resin based on the vegetable oil, AEO was copolymerized with MMA by the similar method to the homopolymerization. The monomer compositions used were 1/1 and 1/4 in the wt % of AEO/MMA, and the concentration of the BPO was 10% of the monomer content, and polymerization temperature and time were 80°C and 24 h, respectively. After completion of the polymerization, the copolymers were purified by the precipitation method in the nonsolvent, such as, ethanol.

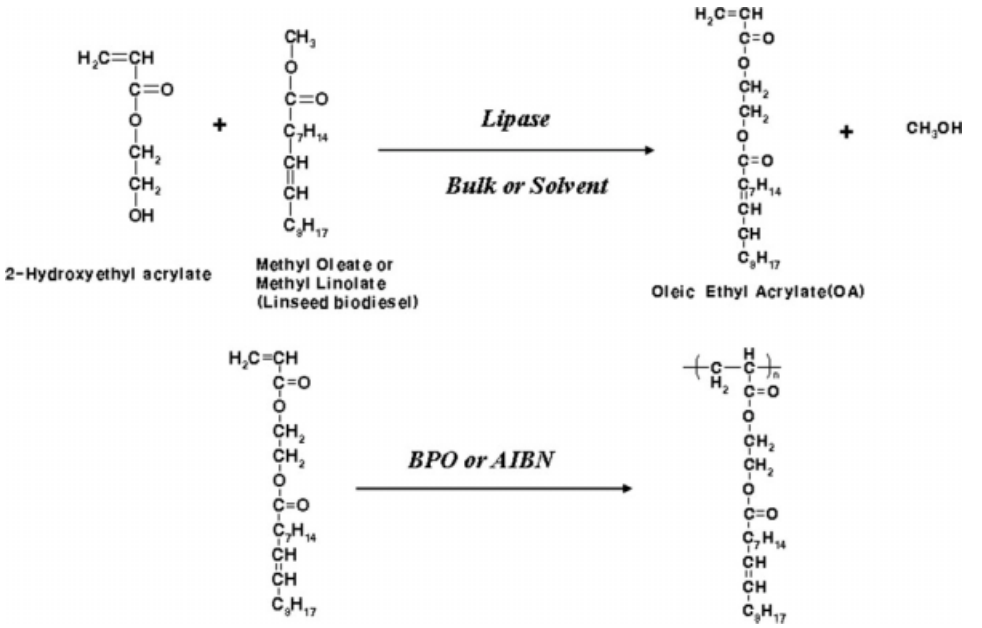
Crosslinking of the copolymers

To see if the AEO homopolymer and copolymers are proper as a coating material, their polymer solutions (solid content: 50 wt %) were prepared by dissolving them in ethyl acetate. The polymer solutions containing MEK-PO (crosslinker) of 3.6 wt % against the resin and Co-Nap (additive) of 1.6 wt % were cast on a glass plate and kept at room temperature for 3 days to crosslink the polymer resins. After which the pencil-hardness of the crosslinked resin was measured (see Table II).

Characterization

High performance liquid chromatograph (HPLC)

To determine the conversion ratio of MO in the transesterification with HEA for the synthesis of the acrylic monomer, HPLC was used: Small amount of reaction solution taken from time to time was mixed with acetonitrile to dilute the solution to 5×10^{-3} g/mL, then the solution was filtered with a PTFE filter with pore size of 0.45 μm. After that the solution was injected into the HPLC and measured the concentration of the MO unreacted. From the concentration of the MO unreacted, the conversion ratio of MO was then calculated.



Scheme 1 Transesterification and polymerization scheme of HEA and MO using lipase catalyst.

Nuclear magnetic resonance (NMR)

To characterize the structure of the monomer and polymer ^{1}H-NMR (300 MHz, Bruker) was used using $CDCl_3$ as a solvent.

Gel permeation chromatograph (GPC)

To measure the molecular weight of the acrylic polymer, GPC was used. PLgel column with 300 × 7.5 mm^2 length was used and the eluent was THF. The flow rate of the eluent was 10 mL/min. The detector used was VE 3580 Refractive Index Detector (Viscotek).

Thermal analysis

Thermal property of the polymer was characterized using differential scanning calorimetry (DSC, DSC 2010). Heating rate was 5°C/min and it was performed under nitrogen. The temperature range scanned was from −50 to 120°C.

Control of water activity

To control the activity (a_w) of the enzymes used, water activity of the enzymes was controlled using various salt solutions: The enzymes, such as, CAL-B, Novozyme-435, Lipo RM IM, and Lipo TL IM were kept at room temperature for 7 days with various saturated salt solution in a desiccant to control the amount of water contained in the enzymes. When different salt solution was used, different water activities were obtained and the water activity of each solution was as a follow: NaOH (a_w = 0.05), LiCl (a_w = 0.11), KCO_3 (a_w = 0.43), and NaCl (a_w = 0.75).[24–26]

RESULTS AND DISCUSSION

Synthesis of an acrylic monomer

Effect of different lipases

For the preparation of the acrylic monomer with long alkyl chain that contains double bond in it, lipase was used as a catalyst for the transesterification reaction of HEA with MO as shown in Scheme 1. In this reaction excess amount of HEA was used to achieve maximum conversion of MO, for the easy purification of the acrylic monomer. After completion of the reaction, the acrylic monomer was purified by the extraction with water of the HEA remained in the solution unreacted.

To select proper lipase catalysts for this transesterification reaction, different lipases, such as, Lipozyme RMIM (immobilized), Lipozyme TLIM (not immobilized), Novozyme-435 (immobilized), and CAL-B (immobilized) were used in this study. The reaction temperatures used for this reaction were 30, 50, 70, and 90°C.

Figure 1 shows the conversion of the MO at different reaction temperatures when different lipases were used. Novozyme-435 lipase showed relatively high conversion in the wide temperature range from 30 to 90°C, indicating that it has good thermal stability. However, CAL-B and RMIM lipases showed low thermal stability, showing large decrease in the conversion at 90°C. When unloaded Lipozyme TLIM was used, the conversion was very low at all the temperature used, indicating loading process of the

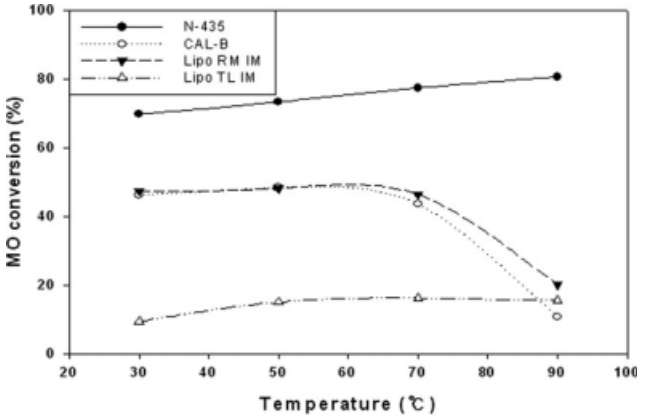


Figure 1 MO conversion in the transesterification reaction with excess amount of HEA at different reaction temperatures when different enzymes were used: (Novozyme-435 (●), Lipozyme RM IM (▼), CAL-B (○), Lipozyme TL IM (△)).

enzyme to be used as catalyst is very important. Generally, when unloaded enzyme is used, enzyme itself forms agglomerate in the reaction solution, decreasing the surface area of the enzyme that interacts with reactants.

From this study, Novozyme-435 lipase was appeared to be the best for our purpose of reaction for the formation of the acrylic monomer.

Effect of water activity (a_w)

It has been known that amount of water contained in the enzyme affect on the activity of the enzyme, because original structure of the enzyme is kept by the water contained in the enzyme. When water is deficient, it causes the shape of the active site of the enzyme to be distorted, resulting in the decrease in the enzyme activity. However, when too much water is contained in the enzyme, the excess amount of water causes hydrolysis instead of the transterification in the reaction solution to occur, decreasing the conversion ratio. So, the amount of water contained in the enzyme is called water activity (a_w), and it has to be controlled for better enzyme activity.

In this study, to control the water activity of the Novozyme-435 four different salt saturated aqueous solutions were used as explained in the Experimental section, such as, NaOH ($a_w = 0.05$), LiCl ($a_w = 0.11$), K_2CO_3 ($a_w = 0.43$), and NaCl ($a_w = 0.75$), and MO conversion versus reaction time as a function of water activity of the Novozyme-435 was obtained as shown in Figure 2. From this study, it was found that high water activities beyond 0.05 for the Novozyme-435 were not good for high MO conversion.

From this data, it can be explained that water activity of 0.05 is high enough for the Novozyem-435 to have high enzyme activity, and excess amount of water contained in the Novozyme-435 making the

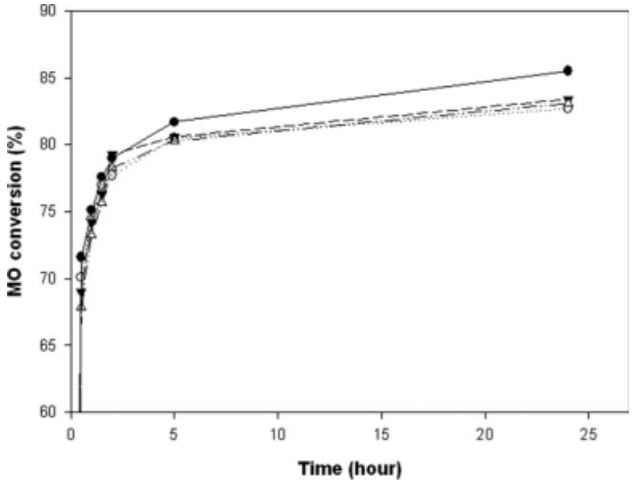


Figure 2 MO conversion with reaction time when Novozyme-435 with different water activity was used: a_w (0.05 NaOH (●), 0.11 LiCl (○), 0.43 KCO_3 (▼), 0.75 NaCl (△)).

water activity beyond 0.05 causes the hydrolysis reaction to occur, which is harmful for the transesterification reaction for the MO conversion, resulting in the low conversion of MO.

Effect of amount of lipase added

Figure 3 shows the MO conversion obtained when different amount of lipase was added into the reaction solution. It is general that as large amount is used, high conversion is achieved. In this study, such kind of result was obtained. With increasing amount of enzyme from 2 to 15 wt %, the MO conversion after 24 h of reaction increased gradually, and reached about 87%.

Effect of the molar ratio of HEA and MO

To find out the best molar ratio between HEA and MO, five different molar ratios were used in this

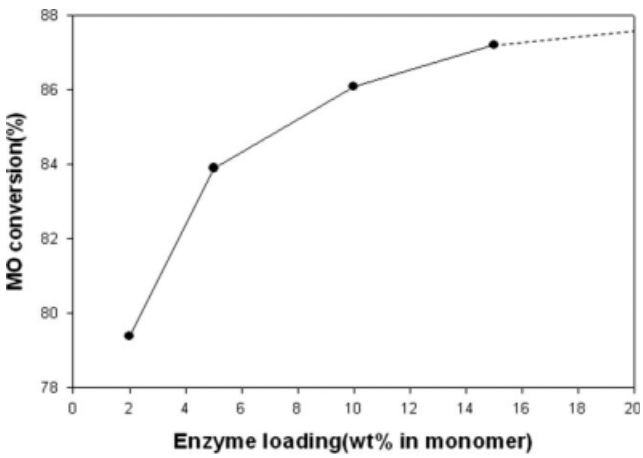


Figure 3 MO conversion after 24 h of reaction with different amounts of enzyme from 2 to 15 wt %.

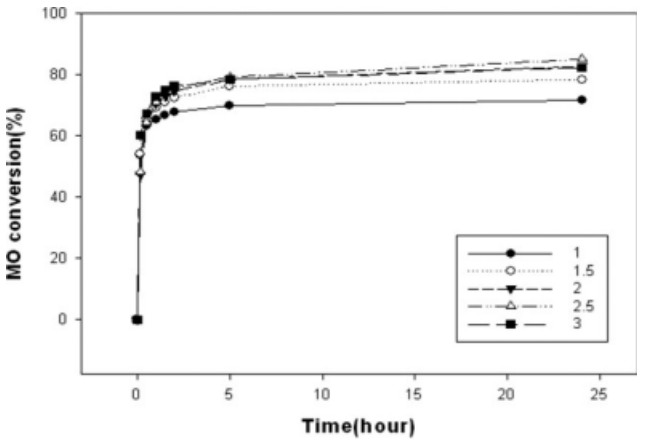


Figure 4 Effect of reaction time on the conversion (%) at different substrate molar ratio (HEA/MO): (HEA/MO = 1.0 (●), 1.5 (○), 2.0 (▼), 2.5 (△), 3.0 (■)).

study: molar ratio between HEA and MO = 1.0, 1.5, 2.0, 2.5, and 3.0. Figure 4 shows the MO conversion according to the reaction time with 15 wt % of Novozyme-435. It was found that when the molar ration was 2.5, the MO conversion was the highest. With increasing molar ratio of HEA against MO, the MO conversion was increased. This result indicates that the intermediate first formed by the interaction between lipase and MO should have high collision frequency with HEA for the completion of the transesterification reaction, because it is possible for the large amount of HEA to have higher possibility to contact with MO.

Identification of the structure of acrylic monomer using ^{1}H-NMR

Figure 5 shows the ^{1}H-NMR spectrum of the acrylic monomer purified by extracting with water the unreacted HEA out of the reaction mixture, followed by drying under vacuum at room temperature. The unreacted MO was impossible to be removed, because the solubility of both MO and acrylic monomer was very similar each other. The ^{1}H-NMR spectrum of the acrylic monomer showed unreacted MO peak at 3.6 ppm (3H, —$COOCH_3$). Other than that every single peak of the spectrum was as assigned in the Figure 5, so that it is confirmed that the acrylic monomer with long alkyl chain came from MO was successfully prepared by using lipase as catalyst.

Polymerization of the acrylic monomer

Effect of concentration of initiator

As explained in the Experimental section, the acrylic monomer with a long alkyl chain prepared in this study was homo-polymerized or copolymerized

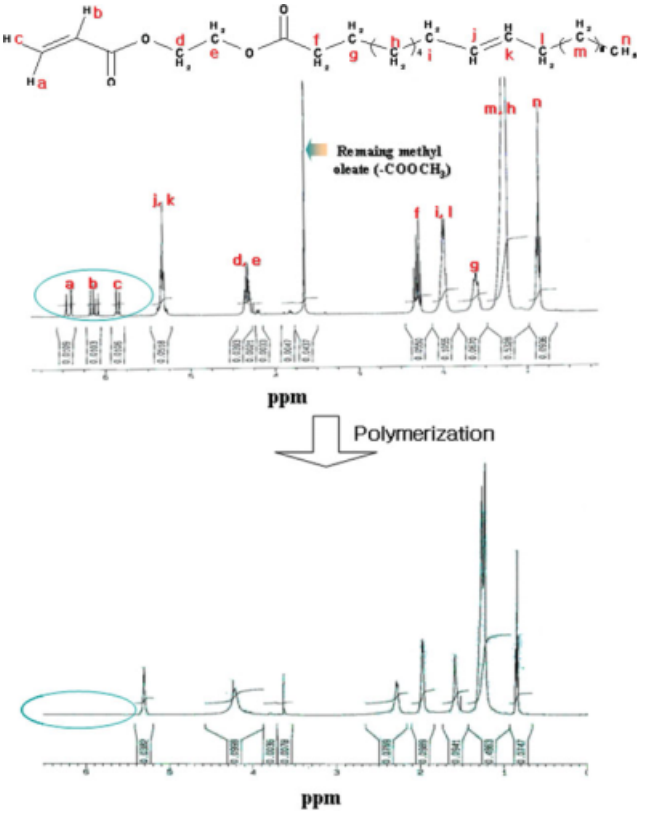


Figure 5 ^{1}H-NMR spectra of the acrylic monomer and its polymer. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

with MMA as comonomer by the radical polymerization using BPO as an initiator. Figure 6 shows the molecular weight of the homo-polymer of AEO as a function of the concentration of initiator. It is general that, in the radical polymerization, the molecular weight of the polymer produced depends on the concentration of the initiator used. Usually as the concentration of the initiator decreases, the

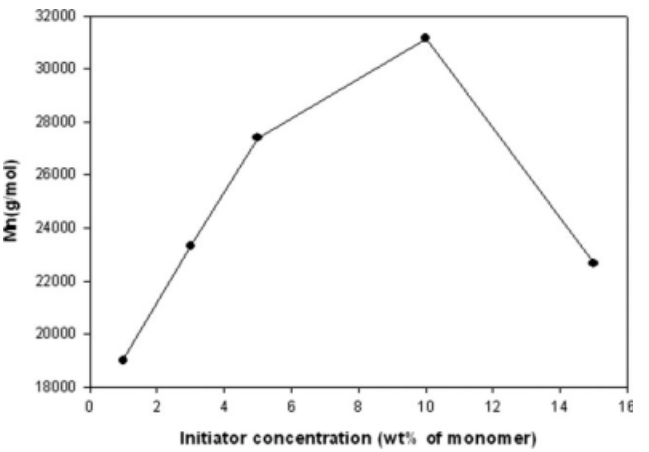


Figure 6 Effect of initiator concentration on the molecular weight of the polymers prepared from different polymerization times.

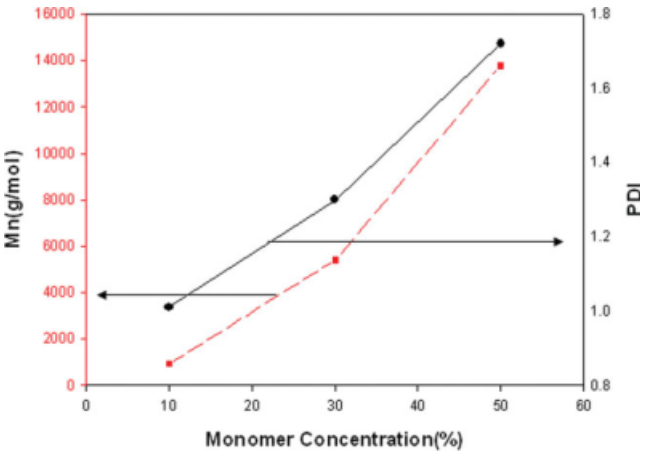


Figure 7 Effect of monomer concentration on the molecular weights (M_n) and polydispersity index (PDI) of the polymers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

molecular weight of the polymer increases. However, what we found in this experiment was different from that. As shown in Figure 6, the molecular weight of the polymer prepared increased with increasing concentration of the initiator up to 10 wt %. Beyond that the molecular weight was decreased again. From this result, it was suggested that the acrylic monomer used in this study was not pure enough. It probably contains trace amount of water, which can act as radical scavenger. Probably, it is thought that such little amount of water consumed the initiator before it worked to polymerize, so that the molecular weight achieved was maximum when the concentration of the initiator was 10 wt % of the amount of the monomer.

Effect of concentration of OA

Figure 7 shows the number average molecular weight of the polymers prepared according to the concentrations of the monomer used. To know the effect of the monomer concentration on the molecular weight of the polymers, the concentration of the monomer was varied: 10, 30, and 50%. As shown in Figure 7, the molecular weight increased with monomer concentration, the polymer dispersity index (PDI) also increased. This kind of phenomenon can be explained by the collision frequency between the monomers. It is generally accepted that for the occurrence of reaction, two molecules have to collide and get together for a certain time. On the basis of this, this result can be understood as the concentration of monomer increased, it is obvious that the more monomers can contact each other for their reaction. In other words, with increasing concentration of monomer, the more monomers with radical initiated by the initiators have more chance to collide with other monomers, before the radical decay by the reaction with other contaminants presenting in the polymerization system, increasing the molecular weight of the polymer being produced. The increase in the PDI with increasing molecular weight is generally accepted result in the polymer science.

Copolymerization with methylmethacrylate

To prepare a resin useful for the coating application, AEO prepared in this study was copolymerized with MMA by the radical polymerization using BPO as the case of homo-polymerization. Table I shows the physical properties of the copolymers prepared from different comonomer compositions. The composition of the AEO of the copolymers were determined using the ^{1}H-NMR by comparing the peak sizes of 3.5 ppm (3H, —OCH_3) from MMA and of 4.2 ppm (4H, —$COOCH_2CH_2OOC$—) from AEO. It was found from the NMR study that the AEO content of the copolymers was only 14.15% and 4.13%, respectively, regardless of the AEO content of comonomer compositions, suggesting that the polymerization rate of AEO was much slower than that of MMA reflecting the effect of heavy molecular weight of the AEO.

Effect of crosslinking on the hardness of the copolymer resin

Table II represents the pencil-hardness of the coating layer of the AEO homopolymer (PAEO) and copolymer (PMA-1) after crosslinking reaction for 3 days at room temperature, using MEK-PO as a crosslinking

TABLE I
Composition and Molecular Weights of Polymers Prepared from Different Monomer Dosage Ratios

Sample name	Dosage ratio (MMA/AE)	Content of AEO (%)[b]	Molecular weight (M_n, g/mol)	Polydispersity index (PDI)
PMA[a]-1	1/1	14.15	24,349	2.05
PMA-4	4/1	4.13	19,763	2.06

[a] Poly(MMA-co-AEO).
[b] Determined by ^{1}H-NMR.

TABLE II
Effect of Crosslinking on the Hardness and Solubility of Copolymer Coatings

No.	Polymer	Crosslinking	Hardness[a]	Solvent test[b]
1	PAEO	Treated	1H	Insoluble
2	PMA-1	Untreated	3H	Soluble
		Treated	3H	Insoluble

[a] Tested by the method of ASTM 3363.
[b] Dipping in toluene.

initiator as explained in the Experimental section. The double bond contained in AEO was found to be crosslinked, not dissolved in toluene after crosslinking reaction. When compared between PAEO and PMA-1, the hardness of the PMA-1 was higher than that of the PAEO, even though the content of the double bond, the crosslinking site, of PAEO was higher. The reason for this kind of phenomenon would be due to the difference of the softness of those polymers. Because the PAEO with long flexible side group is much more soft plastic than the hard PMMA, the hardness of the crosslinked PMA-1 was higher than the soft PAEO homopolymer. From this data, it can be suggested that by incorporating small amount of PAEO with PMMA, a good coating material with a comparable surface hardness can be prepared.

CONCLUSIONS

Vegetable oil can be used for the formation of a functional acrylic monomer. The MO obtained from Linseed oil was successful to modify HEA to make a functional monomer, AEO, with long alkyl chain that contains a photo-crosslinkable double bond. Novozyme-435 was found to be useful for the transesterification reaction between HEA and MO to synthesize AEO. It was possible to form polyacrylate from the AEO by the radical polymerization using BPO as an initiator. However, the molecular weight of the polymer was in the range from 20,000 to 30,000 g/mol, depending on the polymerization conditions. Higher concentration of the monomer was better for the formation of polymers with higher molecular weights. Incorporating AEO into PMMA by the copolymerization of MMA with AEO, a good coating material with a comparable surface hardness can be prepared.

References

1. Park, S. Y.; Kim, Y. H.; Song, B. K. Polym Sci Technol 2005, 16, 342.
2. He, F.; Li, S.; Ganeau, H.; Vert, M.; Zhuo, R. Polymer 2005, 46, 12682.
3. Ahn, Y. G. Enzyme Chemistry; Chungmoongak: Korea, 1997, p 242.
4. Varma, I. K.; Albertsson, A. C.; Ra; Khowa, R.; Srivastava, R. K. Prog Polym Sci 2005, 30, 949.
5. Ghanem, A. Tetrahedron 2007, 63, 1721.
6. Santaniello, E.; Ferraboschi, P.; Grisenti, P.; Manzocchi, A. Chem Rev 1992, 92, 1071.
7. Ha, S. H.; Lan, M. N.; Lee, S. H.; Hwang, S. M.; Koo, Y. M. Enzyme Microb Technol 2007, 41, 480.
8. Park, E. Y.; Sato, M.; Kojima, S. Bioresour Technol 2008, 99, 3130.
9. Ranganathan, S. V.; Narasimhan, S. L.; Muthukumar, K. Bioresour Technol 2007.
10. Zuhair, S. A.; Ling, F. W.; Jue, L. S. Process Biochem 2007, 42, 951.
11. Modi, M. K.; Reddy, J.; Rao, B.; Prasad, R. Bioresour Technol 2007, 98, 1260.
12. Royon, D.; Daz, M.; Ellenrieder, G.; Locatelli, S. Bioresource Technol 2007, 98, 648.
13. Shah, S.; Gupta, M. N. Process Biochem 2007, 42, 409.
14. Nie, K.; Xie, F.; Wang, F.; Tan, T. J Mol Catal B Enzym 2006, 43, 142.
15. Dorado, M. P.; Ballesteros, E.; Lopez, F. J.; Mittelbach, M. Energy Fuels 2004, 18, 77.
16. Gandhi, N. N. JAOCS 1997, 74, 611.
17. Kobayashi, S.; Uyama, H.; Ohmae, M. Bull Chem Soc 2001, 74, 613.
18. Kobayashi, S.; Uyama, H. Curr Org Chem 2002, 6, 209.
19. Namekawa, S.; Uyama, H.; Kobayashi, S. Macromol Chem Phys 2001, 202, 801.
20. Takamoto, T.; Kerep, P.; Uyama, H.; Kobayashi, S. Macromol Biosci 2001, 1, 223.
21. Kikuchi, H.; Uyama, H.; Kobayashi, S. Macromolecules 2000, 33, 8971.
22. Uyama, H.; Kobayashi, S.; Morita, M.; Habaue, S.; Okamoto, Y. Macromolecules 2001, 34, 6554.
23. Hallsworth, J. E.; Nomura, Y. Biotechnol Bioeng 1999, 62, 242.
24. Colombie, S.; Tweddell, R. J.; Condoret, J. S.; Marty, A. Biotechnol Bioeng 1998, 60, 362.
25. Kim, J. E.; Han, J. J.; Yoon, J. H.; Rhee, J. S. Biotechnol Bioeng 1998, 57, 121.
26. Hadair, N. M.; Basri, M.; Rahman, B. M. A.; Razak, C. N. A.; Rahman, N. Z. A.; Salleh, A. B. J Chem Tech Biotechnol 2001, 76, 511.