

Novel Divinyl Monomer for Preparation of Unsaturated Polymers

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ABSTRACT: To simplify the preparation of unsaturated polymers, a new type of divinyl monomer was designed in this article. The double bonds of the divinyl monomer are different not only in reactivity but also in electron density. Based on quantum chemistry calculation, (z)-4-(2-(acryloyloxy)ethoxy)-4-oxobut-2-enoic acid (*cis*-AEOEA) was selected as the nonelectron-donating divinyl monomer in which inactive double bond was electron deficient and can be activated by electron-donating comonomers by forming

charge transfer complex (CTC) copolymerization system. So, *cis*-AEOEA can be used to simplify the preparation of unsaturated polymers and the content of inactive double bonds left in the polymer is controlled by electron-donating ability of comonomers. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3897–3901, 2008

Key words: divinyl monomer; polymerization activity

INTRODUCTION

The properties and performance of polymers depend on the structures of polymers,¹ and monomer structures decide its polymerization activity. The synthesis of polymer containing crosslinkable groups is being more and more explored. This can be achieved by (1) conjugation of vinyl monomers with polymers containing pendant functional groups,^{2–6} (2) polymerization of supramolecular complexes,⁷ and (3) copolymerization with crosslinkers containing multiple unsaturated groups differing in reactivity.^{8,9} But, the first approach is limited by intricacy of technical process, whereas the latter two are limited by the choice of monomers and crosslinkers.

Therefore, a new type of divinyl monomer should be designed to simplify the preparation of unsaturated polymer. The divinyl monomer should not be an electron donator, and their unsaturated double bonds are different not only in reactivity but also in electron density. The inactive double bond is electron deficient and can be activated by electron-donating monomers via formation of charge transfer complex (CTC) copolymerization system. So, the divinyl monomers can be used to prepare unsaturated polymer, and the content of remained C=C

double bonds can be controlled by the electron-donating ability of comonomers.

Accordingly, the main goal of the study was to select the most suitable divinyl monomer from the four designed compounds (see Fig. 1) which could be synthesized by the reaction of hydroxyl (methyl)acrylate with butenedioic acid (BDA), and some typical experiments were done to prove the effect of comonomers on polymerization activity of selected divinyl monomer.

COMPUTATIONAL

The electron density, electron affinity (EA) and ionization potential (IP) of the four designed compounds were calculated to select the most suitable divinyl monomer. In addition, styrene (St), methyl styrene (MSt), acrylic acid (AA), methacrylic acid (MAA), methyl acrylate (MA), methyl methacrylate (MMA), ethyl acrylate (EA), ethyl methacrylate (EMA), butyl acrylate (BA), butyl methacrylate (BMA), vinyl acetate (VA), and maleic anhydride (MAH) were also calculated as references.

All calculations were performed with Gaussian 03¹⁰ using the density functional theory (DFT). The geometry optimizations and vibrational frequencies were performed by the DFT method using the B3LYP function^{11,12} and the 6-31G(d) basis set. Vibrational frequencies were used to characterize stationary points as stable states (number of

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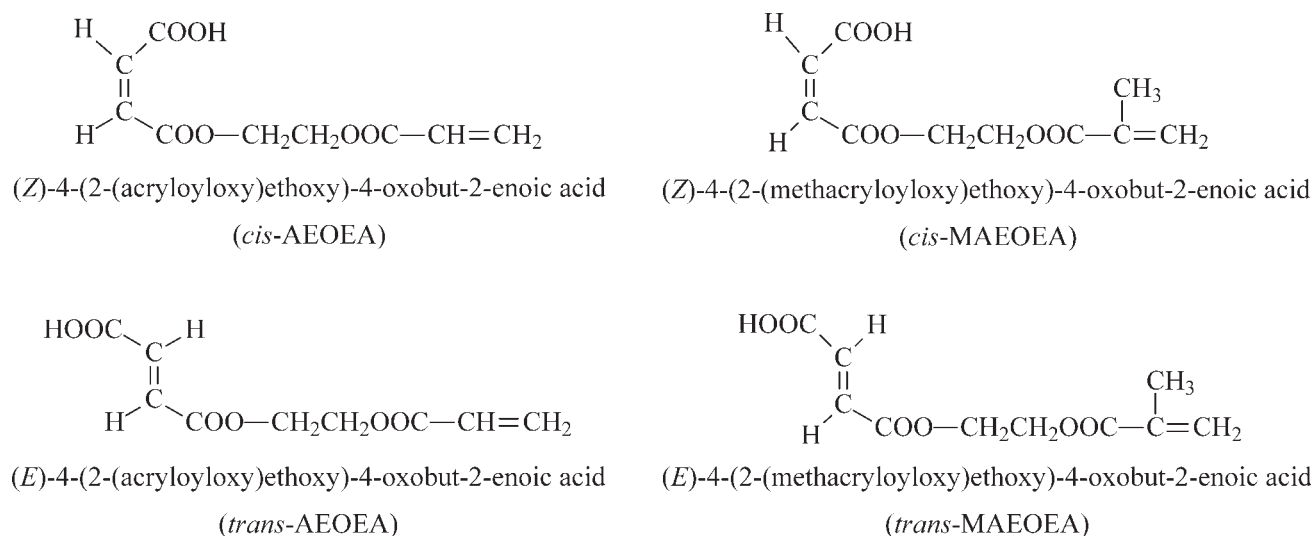


Figure 1 Chemical structure of designed monomers.

imaginary frequencies is 0) and to evaluate zero-point energies (ZPE). Single-point energies (SPE) were computed at B3LYP/6-311+G(2df,3pd) and B3LYP/6-311+G(3df,3pd) level of theory from the optimized stable state. Final energies were calculated at SPE (B3LYP/6-311+G(2df,3pd)) + ZPE (B3LYP/6-31G(d)) and SPE (B3LYP/6-311+G(3df,3pd)) + ZPE (B3LYP/6-31G(d)) level of theory. EA were computed as the energy difference between the neutral and the anion molecule, and IP were computed as the energy difference between the cation and the neutral molecule. Throughout this article, all energies are in hartrees.

EXPERIMENTAL

Materials

VA was purchased from Tianjin Guangfu Fine Chemical Research Institute. BMA was purchased from Tianjin Kermel Chemical Reagents Development Center and was purified by vacuum distillation. *cis*-AEOEA was supported by our laboratory. 2, 2'-Azobisisobutyronitrile (AIBN) was purchased from Aldrich and recrystallized twice by methanol before use. All other chemicals were used as received.

Measurements

FTIR spectra were recorded on a Bruker Tensor 307 FTIR spectrometer using pressed KBr plates.

Synthesis of polymer

The procedure for the solution polymerization of *cis*-AEOEA was done as follows. The *cis*-AEOEA (5 g), AIBN (0.05 g), and ethyl acetate (50 mL) were mixed

in 100 mL three-neck round-bottomed flask with continuous stirring, and polymerized under N₂ atmosphere at 60°C for 1 day. The flask was sealed with rubber septa, attached with a condenser, and kept in a water bath to adjust the temperature to 60°C. Water was added to the final mixture, and an insoluble white solid product was obtained. The white solid was dissolved in ethyl acetate and precipitated into water. The precipitation process was repeated two more times. Finally, the product was dried in a vacuum oven at 60°C for 1 day.

Essentially, the same procedure was used for the solution copolymerization of *cis*-AEOEA with BMA or VA. The *cis*-AEOEA (5 g), BMA (3.32 g) or MMA (2.37 g), AIBN (0.08 g), and ethyl acetate (70 mL) were mixed in 100 mL three-neck round-bottomed flask with continuous stirring and polymerized under N₂ atmosphere at 60°C for 1 day. Water was added to the final mixture and an insoluble white solid product was obtained. The white solid was dissolved in ethyl acetate and precipitated into water. The precipitation process was repeated two more times. The *cis*-AEOEA (5 g), VA (2.01 g), AIBN (0.07 g), and ethyl acetate (70 mL) were mixed and polymerized under N₂ atmosphere at 60°C for 1 day to give white precipitates. Finally, all products were dried in a vacuum oven at 60°C for 1 day.

TABLE I
Electron Density of Comonomer Double Bond

Monomer	Electron density	Monomer	Electron density
St	0.6111	MSt	0.6359
AA	0.5659	MAA	0.6070
MA	0.5704	MMA	0.6087
EA	0.5710	EMA	0.6090
BA	0.5715	BMA	0.6096
VA	0.65035	MAH	0.4644

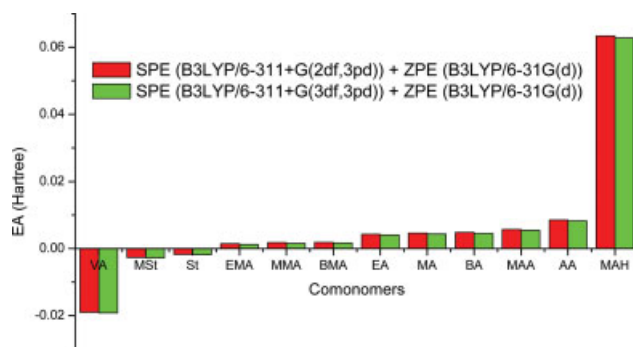


Figure 2 Electron affinities of comonomers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

RESULTS AND DISCUSSION

Electron-accepting and donating properties of vinyl monomers

The electron-accepting and donating properties of typical vinyl monomers were calculated as references to select the most suitable designed monomer. These properties are electron density, EA, and IP which have effects on the formation of CTC. The electron density of C=C double bonds are calculated and listed in Table I.

It can be seen from Table I, the monomers in which double bonds are bonded with methyl have higher electron density. VA has highest electron density, whereas MAH has the lowest electron density. For typical CTC polymerization system—St and MAH, their electron density of double bond are 0.6111 and 0.4644. CTC polymerization system is likely to be formatted between electron-rich and deficient monomers in which electron density of double bonds are beyond 0.6111 ~ 0.4644, and this range will be used as reference for the selection of designed divinyl monomers.

Besides electron density, their EA and IP are also calculated and shown in Figures 2 and 3. CTC copolymerization system is favorable to be formed between monomers with larger EA and smaller IP, respectively.

The larger EA indicates the higher electron-accepting ability. It can be seen from Figure 2 that VA, MSt, and St cannot accept electron because of their

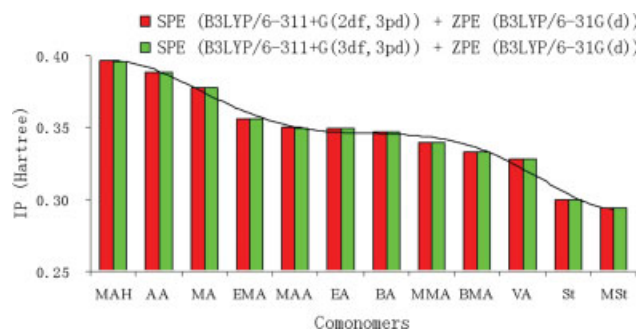


Figure 3 Ionization potentials of comonomers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

negative EA at both calculation levels. MAH has the largest EA, and it is selected as reference electron acceptor for the selection of designed monomers.

The smaller IP indicates the higher electron-donating ability. MAH has the highest IP, whereas MSt has the lowest IP. BMA and VA were selected as reference of electron donor for the selection of designed monomers because of their relative lower IP.

Electron-accepting and donating properties of designed divinyl monomers

To find the most suitable designed monomer to simplify the preparation of unsaturated polymers, electron-accepting and donating properties of the four designed monomers were calculated.

The electron densities of double bonds in designed divinyl monomers are calculated and listed in Table II.

It can be seen from Table II that, for divinyl monomers with the same conformation, the active double bonds have higher electron density which are bonded with methyl, whereas the inactive double bonds have lower electron density with active double bond, in the same divinyl monomer, are bonded with methyl.

In addition, EA and IP of these four designed divinyl monomers are also calculated and shown in Figures 3 and 4.

As seen from Figure 4, *cis* conformation has higher EA when comparing *cis*-AEOEA with *trans*-AEOEA,

TABLE II
Electron Density of Double Bond in Designed Divinyl Monomers

Double bond	Electron density	Double bond	Electron density
<i>cis</i> -AEOEA (active C=C)	0.5925	<i>cis</i> -MAEOEA (active C=C)	0.6243
<i>trans</i> -AEOEA (active C=C)	0.5967	<i>trans</i> -MAEOEA (active C=C)	0.6232
<i>cis</i> -AEOEA (inactive C=C)	0.4674	<i>cis</i> -MAEOEA (inactive C=C)	0.4639
<i>trans</i> -AEOEA (inactive C=C)	0.4787	<i>trans</i> -MAEOEA (inactive C=C)	0.4499

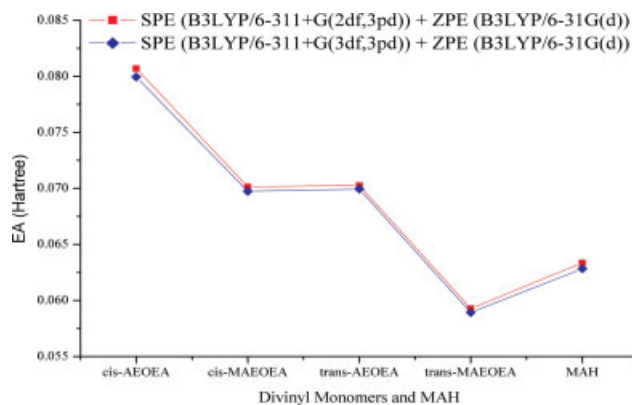


Figure 4 Electron affinities of divinyl monomers and MAH. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

or comparing *cis*-MAEOEA with *trans*-MAEOEA, whereas divinyl monomers in which active double bonds are bonded with methyl have lower EA. MAH is the reference monomer as mentioned earlier.

As seen from Figure 5, *cis* conformation has higher IP when comparing *cis*-AEOEA with *trans*-AEOEA, or comparing *cis*-MAEOEA with *trans*-MAEOEA, whereas divinyl monomers in which active double bonds are bonded with methyl have lower IP. VA and BMA are the reference monomers as mentioned earlier.

Selection of divinyl monomers

To find the suitable divinyl monomer to simplify the preparation of unsaturated polymers, the selected divinyl monomers should be different not only in reactivity but also in electron density, and the inactive double bond should be electron deficient. Moreover the selected divinyl monomer should not be an electron donor against the formation of self-CTC polymerization system.

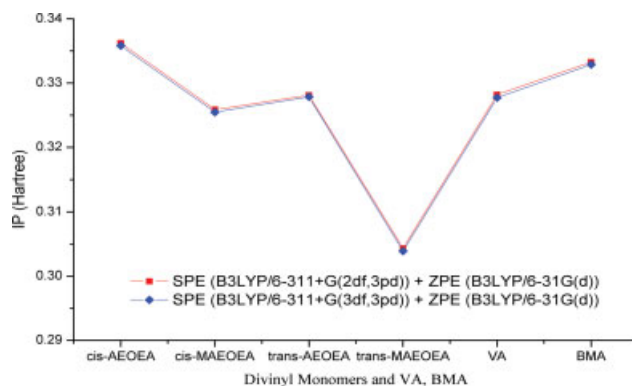


Figure 5 Ionization potentials of divinyl monomers, VA, and BMA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

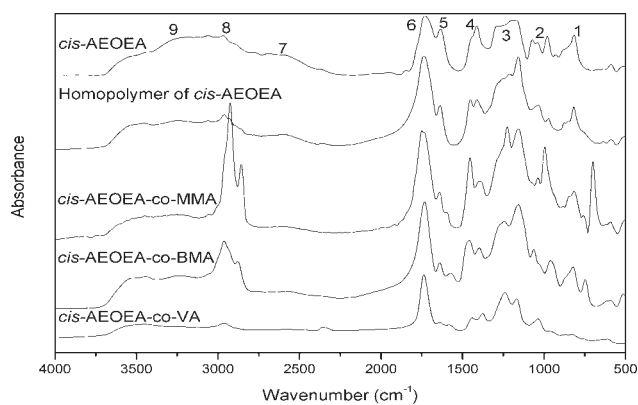


Figure 6 FTIR of *cis*-AEOEA and its polymer.

In the four designed monomers, the electron density of two double bonds were both beyond the range of 0.6111 ~ 0.4644 for *cis*-MAEOEA and *trans*-MAEOEA. In addition, for *cis*-MAEOEA, the EA was higher than MAH, whereas IP was lower than VA and BMA.

Therefore, *cis*-AEOEA is the only designed monomer suitable for simplifying the preparation of unsaturated polymers and the content of remained double bonds can be controlled by electron-donating ability of comonomers by forming CTC copolymerization system. In the following, some typical experiments were performed to study the effect of comonomers on polymerization activity of selected *cis*-AEOEA.

Effect of comonomers on polymerization activity of *cis*-AEOEA

To study the effect of electron-donating ability of comonomers on the polymerization of *cis*-AEOEA, Fourier transform infrared spectroscopy (FTIR) was used to follow the polymerizations (Fig. 6).

The peak assignments for the *cis*-AEOEA monomer were made as follows: 1-C-H out-of-plane bending in CH=CH (821 cm^{-1}), 2-C-O stretching of O-CH₂ (1041 cm^{-1}), 3-C-O-C antisymmetric stretching of O=C-O-C (1175 cm^{-1}), and C-O stretching of O=C=O (1166 cm^{-1}), 4-CH₂- bending and stretching (1420 cm^{-1}), 5-C=C stretching (1635 cm^{-1}), 6-C=O stretching (1735 cm^{-1}), 7-H-bonded COOH (2300 ~ 2850 cm^{-1}), 8-aliphatic CH, CH₂, CH₃ symmetric and asymmetric stretching (2850 ~ 3100 cm^{-1}), 9-H₂O and COOH (3100 ~ 3600 cm^{-1}). The intensity of Peak 1 and Peak 5 decreased and disappeared after polymerization.

The area of Peaks 5 and 6 was fitted using Lorentzian function, and area ratio of Peaks 5 and 6 was defined as the relative content of remained inactive C=C in molecule. The area ratio of *cis*-AEOEA and its polymer are shown in Figure 7, and the

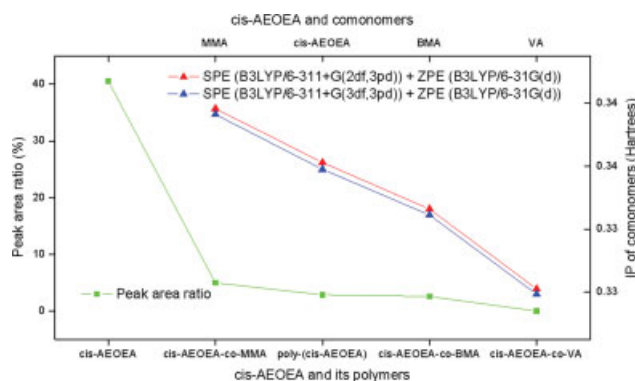


Figure 7 Peak area ratio of *cis*-AEOEA and its polymer and IP of *cis*-AEOEA and comonomers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

corresponding monomers are also shown in descending order of IP.

As seen from Figure 7 that, the ratio of poly(*cis*-AEOEA) is lower than *cis*-AEOEA; therefore, active acrylate double bond of *cis*-AEOEA was polymerized, whereas the inactive double bond was partially left in polymer. The ratio of *cis*-AEOEA-co-BMA is lower than *cis*-AEOEA-co-MMA, and *cis*-AEOEA-co-VA is the lowest (= 0). In addition, the ratio of *cis*-AEOEA-co-MMA should be lower than poly(*cis*-AEOEA) because the content of C=O increases, but the fact is contradicted. This phenomenon indicates that the activation of *cis*-AEOEA is stronger than MMA because of lower IP of *cis*-AEOEA. Thus, the content of remained inactive double bond in poly(*cis*-AEOEA) is lower than *cis*-AEOEA-co-MMA. In sum, from the decreasing of C=C in the polymers, it can be seen that *cis*-AEOEA can be used for the preparation of unsaturated polymers, and the content of inactive double bonds left in polymer are

controlled by the electron-donating ability of comonomers.

CONCLUSIONS

A new type of divinyl monomer was designed. *Cis*-AEOEA is not an electron-donator, and its inactive double bond is electron-deficient and can be activated by electron-donating comonomers by forming CTC copolymerization system. Therefore, *cis*-AEOEA was selected from the four designed divinyl monomer to simplify the preparation of unsaturated polymers, and the content of inactive double bonds left in polymer is controlled by electron-donating ability of comonomers.

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