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Synthesis of guerbet alcohol acrylate aided by microwave

Xu Dong[1,a], Xiaohui Zhang[2,b], Minghui Zhou[3,c], Wenhuan Wang[4,d], Jingchang Wang[5,e*]

[1]Xu Dong, Institute of Chemistry, Dalian University, China

[2]Xiaohui Zhang, Institute of Chemistry, Dalian University, China

[3]Minghui Zhou, PetroChina Sichuan Petrochemical Company Limited, China

[4]Wenhuan Wang, Institute of Chemistry, Dalian University, China

[5]Jingchang Wang, Institute of Chemistry, Dalian University, China
[*]College of Environment and Chemical Engineering, Dalian University, Dalian, China

[a]milksquare@163.com,[b]xiaohuizhang@163.com,[c]Zhouminghui007@163.com,
[d]wangwenhua02@163.com,[e*]wjc6116@163.com

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Introduction

Guerbet alcohol acrylate was synthesized using acrylic acid and guerbet alcohols as reactants, p-toluenesulfonic acid as catalyst, hydroquinone as polymerization inhibitor and toluol as solvent by microwave irradiation heating instead of the conventional heating with oil bath. The structure of product was characterized by FT-IR, 1H-NMR, 13C-NMR and the effect of different reaction parameters was discussed in this paper. A procedure for the generation of fairly clean guerbet alcohol acrylate is well developed and the results indicated that under the appropriate reaction conditions the esterification rate of guerbet alcohol acrylate could be achieved above 98%.

The synthesis of acrylate is often based on the traditional heating method, whereas, the synthesis of guerbet alcohol acrylate was studied by microwave heating [1-3] in this paper. Recently, the microwave irradiation technique has been introduced as a well-established, economic, and energy efficient method of expediting the chemical reactions [4]. Microwave heating is the first new heating technique in the millions of years since the discovery of fire. This kind of heating method is based on the ability of some liquids and solids to transform electro-magnetic energy into heat and it has revolutionized cooking and chemistry applications. And the method has the advantages of mild condition, few side reactions, high yield, short reaction time and no thermal decomposition of products [5].

As there is no systematic study on the synthetization of guerbet alcohol acrylate conducted in a microwave chemistry reactor in the previously reported literature. And in this paper, the microwave-assisted method is suitable for the synthesis of guerbet alcohol acrylate, including 2-Butyloctyl acrylate, 2-Amylnonyl acrylate, 2-Hexyldecyl acrylate, 2-Heptylhendecyl acrylate and 2-Octyllauryl acrylate. The representative compound of 2-Hexyldecyl acrylate was studied by discussing the synthetic method, reaction conditions and the effect of different reaction parameters.

Materials and Apparatus

Acrylic acid was supplied by the Tianjin Kermel Chemical Reagent Company. guerbet alcohol alcohols obtained from Aldrich. p-toluenesulfonic acid, hydroquinone and toluol were supplied by the Tianjin Damao Chemical Reagent Factory. Acrylic acid and guerbet alcohol alcohols were of the highest purity available. The other chemicals were all analytical grade.

The esterification reaction was performed in MCR-3 domestic microwave chemistry reactor. The FTIR spectrums of 2-Hexyldecanol (Fig.1a) and of 2-Hexyldecyl acrylate (Fig. 1b) were recorded in solid state, by KBr pellet method, using a FTIR spectrophotometer (Model IR-Prestige21, Shimadzu Corpo-ration, Japan) between 400 and 4000 cm^{-1} . ^{1}H-NMR and ^{13}C-NMR spectra of the samples were run on a Bruker 320 MHz spectrophotometer. Spectra were recorded at room temperature as 15–20% (w/v) solution of $CDCl_3$/DMSO-d_6 (Aldrich) with TMS as an internal standard. The protons were decoupled from ^{13}C nuclei by broad band irradiation.

Synthesis of 2-Hexyldecyl acrylate

The synthetic process was carried out in microwave reactor. The given amount of purified Acrylic acid(9.36g, 0.13mol), 2-Hexyldecanol(24.2 g, 0.1 mol), p-toluenesulfonic acid(0.6g, mass fraction of 1.8%,), hydroquinone(0.27g, mass fraction of 0.8%) and toluol(17mL, mass fraction of 50%) were placed in a dry and clean three-necked flask. Because the speed of microwave heating is so quick that the acrylic acid had polymerized before the polymerization inhibitor completely dissolved in the reaction system. In order to avoid the polymerizing occured prematurely, it should be heated in water bath of 60˚C to ensure the polymerization inhibitor could be dissolved before microwave irradiation. Subsequently, the reaction vessel was placed on the turntable of a microwave oven, with a temperature sensor inserted in the three-necked flask. The desired temperature and revolving speed were maintained at 128˚C and 900 seconds, respectively. The toluene was continually evaporated and the water in this system was removed by a water segregator. About 15 minutes later, the completion of raw product was obtained. The esterification rate was calculated by measuring the volume of collected water. The unreacted acrylic acid, p-toluenesulfonic acid and hydroquinone were washed away with 5% sodium hydroxide solution, and then washed with saturated sodium chloride solution to neutralize redundant alkali until the PH closed to 7. Finally, the obtained product was dried under vacuum for 12h.

Characterization

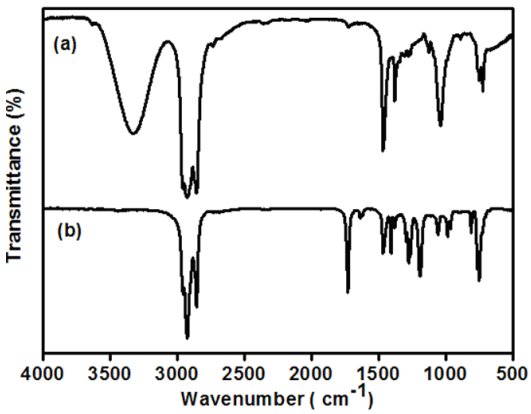

Fig. 1. FTIR spectrum of (a) 2-Hexyldecanol and (b) 2-Hexyldecyl acrylate

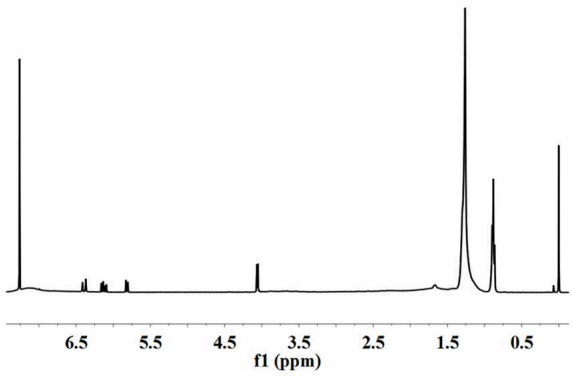

Fig. 2. ^{1}H NMR spectrum of 2-Hexyldecyl acrylate

From the FTIR spectrum of 2-Hexyldecanol (Fig. 1a), it has been observed that a peak at 3322 cm^{-1} is due to stretching vibration of –OH ($C_8H_{17}(C_6H_{13})CHCH_2OH$), peaks at 2925 cm^{-1} and 2854 cm^{-1} are assigned to the methyl C-H stretching vibrations. The peak at 1466 cm^{-1} is due to the C-C bending vibration.

In case of 2-Hexyldecyl acrylate (Fig. 1b), it has been observed that there are some additional peaks. C=O absorbs at 1729 cm^{-1}. CH_2=CH– stretching at 1636.14 cm^{-1}. Peak at 1274 cm^{-1} and 749 cm^{-1} are due to the C-O stretching vibration. The C–O–C stretching appears at 1190 cm^{-1}. By contrast, the peak at 3322 cm^{-1} is disappeared. These extra and disappeared peaks in case of 2-hexyl

decyl acrylate are well explained by the presence of ester group and are confirmations of the intended esterization method.

Fig. 2 shows a typical ^{1}HNMR spectrum of 2-Hexyldecyl acrylate. The characteristic chemical shifts at δ= 5.82-6.39 ppm correspond to terminal olefine protons in the main chain of 2-Hexyldecyl acrylate. The signals at δ=4.06 ppm correspond to methine protons. There is no signal due to the hydroxy group protons and the carboxy groupthe hydroxy group protons.

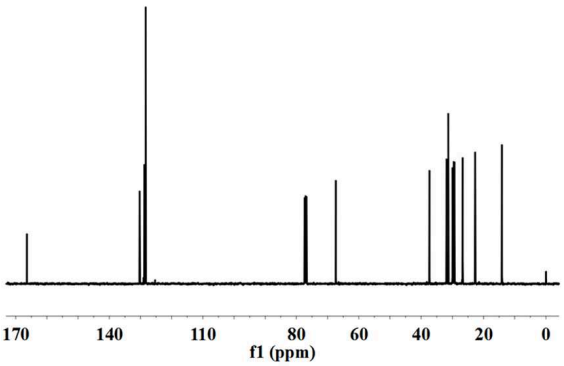

Fig. 3. ^{13}C NMR spectrum of 2-Hexyldecyl acrylate

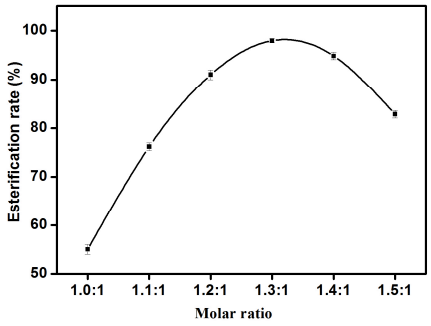

Fig. 4. Relationship of esterification rate with the molar ratio of acrylic acid and 2-Hexyldecano

The carbon atoms of 2-Hexyldecyl acrylate are identified and are represented in Fig. 3. The signals at δ=166.4 ppm appear as singlet (C=O); The signals at δ=128.32-128.44 ppm appears as a triplet (CH_2=), The signals at δ=128.73 -130.27 ppm appears as a doublet (–CH=); The signals at δ=67.36 ppm due to methine carbon atom appears as a singlet.

Results

The esterification rate calculation. The esterification rate (%E) of this microwave assisted synthesized guerbet alcohol acrylate was calculated as:

$$\%E = \frac{Wt.\ of\ the\ actural\ water\ yield}{Wt.\ of\ the\ theory\ water\ yield} \times 100\%$$

The esterification rate of guerbet alcohol acrylate was over 98%.

The effect of different reaction parameters. The effect of raw material molar ratio, esterification time, reaction temperature, and the amount of catalyst, inhibitor and solvent on esterification rate was investigated. They were the important reaction parameters in the esterification, and the experimental results explained that the esterification rate was effectively increased under the appropriate reaction conditions.

The relationship of esterification rate with the molar ratio of acrylic acid to 2-Hexyldecanol is displayed in Fig. 4. It is easy to see that the esterification rate increases gradually, and when the molar ratio is higher than 1.3:1, the esterification rate begin to reduce. So, it shows a good esterification rate when the molar ratio is 1.3:1.

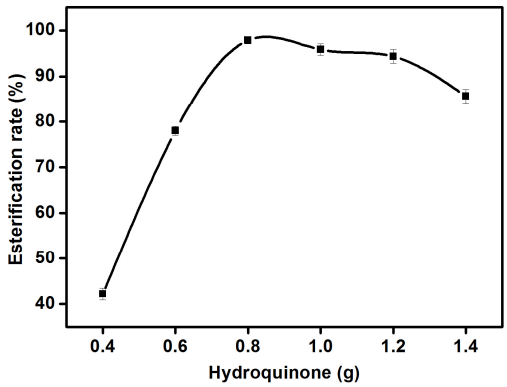

Fig. 5. Relationship of esterification rate with the quantity of hydroquinone

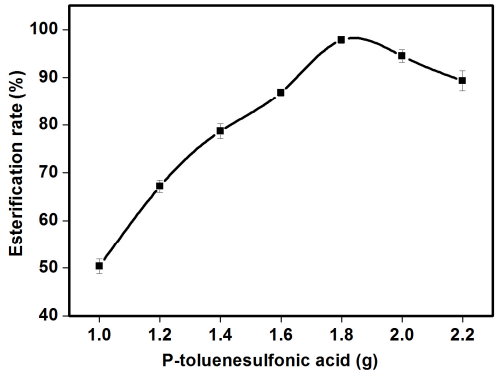

Fig. 6. Relationship of esterification rate with the quantity of p-toluenesulfonic acid

The relationship of esterification rate with the amount of hydroquinone is illustrated in Fig. 5. A moderate increase of hydroquinone is helpful for the improvement of the workability of esterification. But a higher inhibitor will become more difficult to remove. Consequently, proper amount of hydroquinone is necessary, and when the addition of hydroquinone is 0.8%(in the total amount of acrylic acid and 2-Hexyldecanol), esterification rate is the highest.

Figure 6 is the change of esterification rate with the amount of p-toluenesulfonic acid. As observed in this figure, with the addition of p-toluenesulfonic acid, the esterification rate increases significantly. Whereas excess catalyst needs to be wiped off by much alkali, it will result in the reduction of many esters. Hence moderate catalyst could increase esterification rate, when the p-toluenesulfonic acid addition is 1.8% of total materials, the esterification rate is optimal.

The illustrates the relationship of esterification rate with the temperature of reaction. The boiling point of toluene is 110.6˚C, so that the temperature of esterification should be higher than it, it isn't only as solvent, but also as co-boiling reaegent. According to the variation tendency of the esterification rate with the temperature, 128˚C is confirmed to be the best condition for the esterification.

The relationship of esterification rate with reaction time is revealed, that the esterification rate increases with the reaction time at first, nevertheless the reaction time shouldn't last long, because of the side reactions. There was a maximum esterification rate when the reaction time was near 15min. Hence 15min is the best condition for the esterification.

Conclusions

2-Hexyldecyl acrylate has been synthesized by microwave assisted technique. Microwave-assisted esterifications are quite fast, so it is convenient to study the effects of different reaction parameters on the quality of esterification products and to optimize conditions in a reasonably short time frame. The reaction conditions and method which we have introduced can be effectively used in the synthesization of guerbet alcohol acrylate. And the synthesized guerbet alcohol acrylate was characterized through various physicochemical techniques. Meanwhile the esterification rate of them is over 98% which is higher than others' study. Furthermore this can potentially be an alternate methodology for the preparation of important industrial monomers. Guerbet alcohol acrylate will be a new kind of acylate monomer which can widely used by industrial applications including paints and coatings, textiles, paper, glazing, medicine, optics and oil additives.

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