



# Synthesis, structure and phase transition property of acrylic acid grafted paraffin



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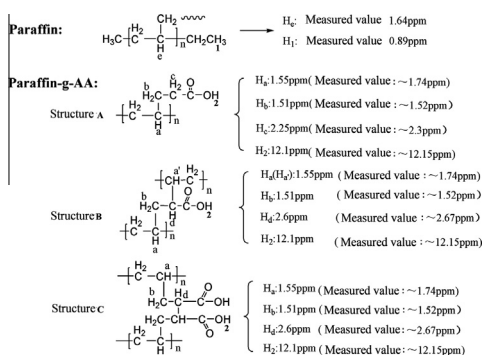
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## HIGHLIGHTS

- AA was used to modify paraffin and improve its latent heat capacity effectively.
- The composition and sequence structure of the grafted products were characterized.
- The mechanism of free radical grafting of AA may be monomeric grafts.
- With increasing grafting ratio, the primary structure of grafts varied from B to A.

## GRAPHICAL ABSTRACT

Polar monomer acrylic acid (AA) was used to modify paraffin in order to improve the latent heat of paraffin as phase change materials. The composition and sequence structure of the grafted products were characterized, and three types of possible grafted products may be obtained during grafting. The proposed chemical structure of paraffin-g-AA and the calculated chemical shifts of  $^1\text{H}$  NMR were shown as below:



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## ABSTRACT

Polar monomer acrylic acid (AA) was used to modify paraffin in order to improve the latent heat of paraffin as phase change materials. The composition and sequence structure of the grafted products were characterized by FTIR,  $^{13}\text{C}$  NMR,  $^1\text{H}$  NMR and GPC analysis, and the thermal properties of paraffin-g-AA were investigated. It was found that AA was confirmed to be grafted onto the molecular chain of paraffin successfully. The mechanism of free radical grafting of AA may be only monomeric grafts. At low grafting ratio, the structure B can be mainly formed as a result of the radical coupling termination; while at the high grafting ratio, structure A was the primary structure as a result of the radical chain growth process. The number-average molecular weight of the grafted samples increased at first but leveled off with increasing grafting ratio, while the weight-average molecular weight increased gradually. The latent heat capacity of the grafted paraffin can be improved obviously at low grafting ratio due to the formation of structure B.

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## 1. Introduction

Heat storage systems are utilized in energy recovery and conservation processes, such as solar heat storage systems. Of various methods of heat storage, latent heat storage is the most

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attractive one due to its high storage density and small temperature variation from storage to release. In such a system, energy is stored during melting and recovered during freezing for a phase change material (PCM) [1].

Several candidates inorganic and organic PCMs and their mixtures have been studied recently for use as latent heat storage materials [2–5]. Among the investigated PCMs, paraffins have been used as the most promising thermal energy storage materials because of their high latent heat and many desired thermal characteristics, such as little or no supercooling, low vapor pressure, thermal and chemical stability and self nucleating behavior [6–7].

However, the nonpolarity of the molecules resulting in very low surface energy and poor adhesive performance is the major drawback of the paraffins as PCMs. At present, grafting of functional monomers onto polymers is an important method for the preparation of high performance materials, which is also the usually used method to enhance the properties of paraffins [8–9]. In order to improve the phase change temperature and latent heat of paraffin, Cuiling Sun et al. used acrylic acid (AA) and methyl methacrylate (MMA) to modify the paraffin, which can be used as infrared stealth material [10]. Haiming Zhang et al. studied the grafting synthesis technique of maleic anhydride (MAH) grafted paraffin using BPO as initiator and the results showed that the grafting temperature was the most important factor that affected the graft ratio, followed by the content of MAH and reaction time [11]. Li et al. discussed the application of maleic anhydride grafted polyethylene wax in filled plastics as a novel coupling agent instead of titanate and aluminate coupling agents [12]. Although abundant information can be available on grafting modification of paraffin, little work has been done on the grafting mechanism and sequence structure of the grafted paraffin.

In this work, the polar monomer acrylic acid was used to modify paraffin in order to improve the adhesive performance and latent heat of paraffin. The sequence structure of the grafted product was characterized for the purpose of detecting the mechanism of the peroxide initiated grafting for paraffin. And the effect of grafting ratio on the phase transformation characteristics of paraffin was investigated.

## 2. Experimental

### 2.1. Materials

Paraffin with melting temperature of  $\sim 76^\circ\text{C}$  was supplied by China academy of engineering physics. Acrylic acid (AA), a commercial product of Bodi Chemical Co. Ltd. (Tianjin, China), was purified by recrystallization from chloroform before use. Benzoyl peroxide (BPO) was supplied by Taizhou Chemical Co. Ltd. (Jiangsu, China) and it was used as received.

### 2.2. Synthesis of acrylic acid grafted paraffin (paraffin-g-AA)

A mixture of AA and BPO as initiator was added at 30-s intervals to the molten paraffin. The reactions were carried out at  $170^\circ\text{C}$  under a nitrogen atmosphere. The product solution was cooled to room temperature and acetone was added to precipitate the grafts. To separate out paraffin-g-AA, the mixed product were dissolved in xylene and the solution was then filtered. The xylene-soluble (grafted) product (paraffin-g-AA) in the filtrate was extracted for five times by using cold acetone.

### 2.3. Measurements

#### 2.3.1. FTIR analysis

The compositions of the synthesized paraffin-g-AA were analyzed with a Nicolet-560 Fourier-transform infrared spectrometer

(FTIR) (USA). The specimen was prepared by casting a polymer film from solution on KBr discs. The scanning rate was  $20\text{ min}^{-1}$ .

#### 2.3.2. $^1\text{H}$ NMR analysis

$^1\text{H}$  NMR measurements of paraffin-g-AA samples were performed with VARIAN INOVA-400 NMR spectrometer (USA). The DMSO- $d_6$  solution of paraffin-g-AA samples with mass fraction of 5% was prepared. The test was operated at room temperature and a frequency of 400 MHz.

#### 2.3.3. $^{13}\text{C}$ solid-state NMR analysis

$^{13}\text{C}$  solid-state NMR measurements were performed on a Bruker AV400 spectrometer operating at 400 MHz. In the measurement, cross-polarization (CP) techniques and proton-decoupling were combined with magic-angle spinning (MAS) in order to obtain high-resolution  $^{13}\text{C}$  spectra. In cases of overlapping signals, the separation of the signals was carried out using PeakFit software (version 1.00, Jandel Scientific, San Rafael, CA).

### 2.4. GPC analysis

The number ( $\overline{M}_n$ ) and weight ( $\overline{M}_w$ ) average molecular weights, and the index of the molecular weight distribution ( $\overline{M}_w/\overline{M}_n$ ) of paraffin-g-AA were measured by gel permeation chromatography (GPC) with a Waters 150-C instrument (USA) at  $30^\circ\text{C}$ . Tetrahydrofuran (THF) was used as an eluent (flow rate = 1 ml/min).

### 2.5. DSC analysis

Thermal properties such as melting temperature and latent heat capacity of pure paraffin and paraffin-g-AA were measured using a DSC instrument (Netzsch 204 Phoenix DSC (Germany)). Indium was used as a reference material for the calibration of the instrument. Samples of about 5–10 mg were heated from ambient temperature to  $100^\circ\text{C}$  at a constant rate of 10 K/min. After holding for 5 min to eliminate the effect of the previous thermal history, the samples were cooled to ambient temperature at a rate of 10 K/min and then the samples were heated to  $100^\circ\text{C}$  with the same constant rate.

### 2.6. Determination of grafting ratio

To determine the grafting ratio, about 2 g of paraffin-g-AA was heated for 2 h in 200 ml of refluxing xylene. This solution was then titrated immediately with a 0.01 N ethanolic NaOH solution with phenolphthalein used as an indicator. The grafting ratio was calculated as below:

$$\text{Grafting ratio (\%)} = \text{MCV}/10m$$

where  $M$  is the molecular weight of grafting monomer, g/mol;  $C$  is the concentration of ethanolic NaOH solution, mol/L;  $V$  is the consumption volume of the standard titrating solution, ml;  $m$  is the weight of the sample, g.

## 3. Results and discussion

### 3.1. Chemical structure of paraffin-g-AA

Acrylic acid (AA) was covalently grafted onto the chain of paraffin by a free radical reaction with BPO as the initiator. Fig. 1 showed the FTIR spectra of paraffin and paraffin-g-AA. For the sample of virgin paraffin, the absorption bands at  $2918$  and  $2849\text{ cm}^{-1}$  were attributed to the asymmetric and symmetric vibrations of methylene ( $-\text{CH}_2-$ ), and the absorption band at  $1473\text{ cm}^{-1}$  was attributed to the deformation vibration of methylene ( $-\text{CH}_2-$ ) or

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