Synthesis, characterization and thermal properties of homo and copolymers of 3,5-dimethoxyphenyl methacrylate with glycidyl methacrylate: Determination of monomer reactivity ratios

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ABSTRACT

The new methacrylic monomer, 3,5-dimethoxyphenyl methacrylate (DMOPM) was synthesized by reacting 3,5-dimethoxyphenol dissolved in ethyl methyl ketone (EMK) with methacryloyl chloride in presence of triethylamine as a catalyst. The homopolymer and copolymers of DMOPM with glycidyl methacrylate (GMA) were synthesized by free radical polymerization in EMK solution at 70 ± 1 °C using benzoyl peroxide as a free radical initiator. The copolymerization behaviour was studied in a wide composition interval with the mole fractions of DMOPM ranging from 0.15 to 0.9 in the feed. The homopolymer and the copolymers were characterized by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopic techniques. The solubility was tested in various polar and non-polar solvents. The molecular weight and polydispersity indices of the polymers were determined using gel permeation chromatography. The glass transition temperature of the copolymers increases with increase in DMOPM content. The thermogravimetric analysis of the polymers showed that the thermal stability of the copolymer increases with DMOPM content. The copolymer composition was determined using ^{1}H NMR spectra. The monomer reactivity ratios were determined by the application of conventional linearization methods such as Fineman–Ross ($r_1 = 0.520$, $r_2 = 2.521$), Kelen–Tudos ($r_1 = 0.629$, $r_2 = 2.554$) and extended Kelen–Tudos methods ($r_1 = 0.600$, $r_2 = 2.502$).

1. Introduction

Beta methoxy acrylate antibiotics (MOAs) represented by strobilurins and oudemansns are known as highly potent antifungal compounds, which are mainly applied to agricultural disinfectants in many countries [1]. Pharmaceutical application studies of these new types of MOAs in the antifungal, antitumor and antimalarial fields based on their structure–activity relationship (SAR) are recently investigated [2–4]. Methoxy methacrylate derivatives were also used as an antifouling agent [5]. The incorporation of different chemical groups in macromolecular chain can be performed by copolymerization reaction between two different monomers. Copolymerization is the most successful method adopted for the preparation of materials with tailor-made properties [6–10]. Glycidyl methacrylate (GMA) enters into a vast number of chemical reactions by opening their oxirane ring, thus offering an excellent opportunity for chemical modification in pendant copolymers. They have also acquired prime importance in various avenues of industrial applications such as leather adhesives, pharmaceutical use for drug delivery [11], pressure sensitive adhesives [12], dental composites [13], superabsorbents [14], non-linear optical materials [15], etc. Aromatic acrylates and methacrylates are highly reactive monomers due to the presence of aromatic ring and thus form an interesting class of polymers. Poly(phenyl methacrylates) possesses high tensile strength, high thermal stability and their glass transition temperatures are higher than their corresponding acrylate polymers, due to the presence of α-methyl group on their main chain. So they find wide applications in the preparation of materials such as photo luminescent [16], photo resist [17], adhesives for leather [18–20], photosensitive [21], biomaterials [22,23], optical telecommunication materials [24], polymer supported catalyst [25], etc. Generally, the conventional epoxidized resin adhesives have molecular weight values around 5000 and are mainly based on phenolic intermediates. They do not have necessary colour stability, possess only a few terminal epoxy groups and require polar solvents for solubilization. Hence, these difficulties were overcomes by taking epoxide containing comonomer (GMA), because of its striking properties.

Monomer reactivity ratio is one of the most important parameters involved in copolymer equation, which can offer detail information regarding relative reactivity of monomer pairs, elucidation of copolymer structure, copolymer composition and monomer sequence distribution. The calculation of the monomer

reactivity ratios mainly requires the mathematical treatment of copolymer composition data. The accurate estimation of copolymer composition and determination of monomer reactivity ratios would be very helpful to synthesize tailor-made copolymers possessing desired properties. In the past few decades, ^{1}H NMR spectroscopy analysis has been established as a powerful tool for determination of tacticity, sequence distribution and as well as for estimation of copolymer composition because of its simplicity, rapidity and sensitivity [26–31]. The presence of aromatic side substituents instead of aliphatic residues in polyacrylic chains gives rise to noticeable effect on the splitting of the NMR signals of several acrylic systems. The main aim in commercial copolymerization is to achieve a product having narrow composition as much as possible. Knowledge about the monomer reactivity ratios of the comonomers would be helpful in achieving this.

We have already reported the monomer reactivity ratios of 3,5-dimethoxyphenyl methacrylate (DMOPM) with methyl methacrylate (MMA) [32]. In continuation, we synthesized and characterized this novel polymeric material for industrial applications. The main aim of this present work is to synthesize and characterize a new monomer 3,5-dimethoxyphenyl methacrylate (DMOPM), its homopolymer and copolymers with epoxy monomer GMA. The present article mainly reports the synthesize, characterization and determination of monomer reactivity ratios of copolymers of DMOPM with GMA. The thermal properties of the polymers were also reported.

2. Experimental

2.1. Materials

3,5-Dimethoxy phenol (Wako Chemical Industries, for synthesis) was used as received. GMA (Wako Chemicals) was purified by distillation under reduced pressure. Benzoyl peroxide (Acros) was recrystallised from chloroform–methanol (1:1) mixture. All the solvents were purified by distillation under to their use. Triethylamine (Wako), methacrylic acid (Wako) and benzoyl chloride (Wako) were used as such. All the other solvents were purified by distillation prior to their use.

2.2. Measurements

Infrared spectra were recorded with a Jasco 460 FT-IR spectrophotometer as KBr pellets. ^{1}H NMR spectra of the monomer and all the polymer samples were run on a JEOL–JNM-LA 400 FT-NMR spectrophotometer at room temperature using CDCl$_3$ solvent and TMS as an internal standard, respectively. The proton decoupled ^{13}C NMR spectrum was run on the same instrument operating 100 MHz at room temperature, and the corresponding chemical shifts were recorded under similar conditions. The molecular weights (M_w and M_n) were determined using Shimadzu gel permeation chromatograph, where tetrahydrofuran was used as an eluent with polystyrene standards for calibration. Thermogravimetric analysis was performed with Shimadzu DTG-50 thermal analyzer in air at a heating rate of 10 °C/min. The glass transition temperature was determined with Shimadzu DSC differential scanning calorimeter at a heating rate of 10 °C/min.

2.3. Synthesis of 3,5-dimethoxy methacrylate (DMOPM)

Methacryloyl chloride was prepared from methacrylic acid and benzoyl chloride using the procedure of Stampel et al. [33]. The synthesis of 3,5-dimethoxyphenyl methacrylate was already reported [32]. The monomer was examined by FT-IR and ^{1}H NMR spectra as follows:

IR cm^{-1}; 3112 and 3102 (=C–H), 2935 and 2839 (C–H stretching), 1735 (C=O), 1677 (CH$_2$=C), 1586 and 1402 (aromatic C=C), 1396 (CH$_3$ symmetrical bending), 1112 (C–O), and 822 and 682 (C–H out of plane bending).
^{1}H NMR; 6.50 and 6.34 (aromatic protons), 6.26 and 5.76 (CH$_2$=C), 3.46 (aromatic-OCH$_3$), and 2.04 (α-CH$_3$).

2.4. Homopolymerization

One gram of monomer DMOPM and 50 mg of BPO free radical initiator were dissolved in 10 ml of EMK in a polymerization tube and oxygen free nitrogen was purged through a solution for 20 min. Then the solution was thermostated at 70 ± 1 °C. After 10 h the polymer was precipitated in methanol. By repeated reprecipitation by methanol from chloroform solution the polymer was reprecipitated. The polymer was then dried in vacuum at 50 °C for 24 h.

2.5. Copolymerization

Predetermined quantities of DMOPM, GMA with EMK and benzoyl peroxide were taken in a standard polymerization tube and the mixture was flushed with oxygen free nitrogen for 20 min. The tube was then tightly sealed and immersed in an oil bath maintained at 70 ± 1 °C. After the required time, the polymer was precipitated in excess methanol. The precipitated polymer was filtered off and purified by repeated reprecipitation from chloroform solution using methanol and finally dried in vacuum at 50 °C for 24 h. The copolymer conversions were restricted to less than 10%.

2.6. Solubility studies

Solubility of the polymers was tested in various polar and nonpolar solvents. About 5–10 mg of the polymer was added to about 4 ml of the solvent in a test tube and kept overnight with the tube tightly closed. The solubility of the polymers was noted after 24 h.

3. Results and discussion

3.1. Synthesis of polymers

Poly(DMOPM) was obtained by the free radical solution polymerization of the monomer at 70 ± 1 °C in EMK solvent using BPO as the initiator. The copolymerization of DMOPM with GMA in EMK solution was studied in a wide composition interval with the mole fractions of DMOPM ranging from 0.15 to 0.9 in the feed. The reaction time was selected in trials to give conversions less than 10% in order to satisfy the differential copolymerization equation. The monomeric units of the copolymer are shown in Scheme 1. The data on composition of feed and copolymers are presented in Table 1.

The homopolymer and the copolymers were soluble in chloroform, acetone, dimethyl acetamide, dimethyl formamide, dimethyl sulfoxide, tetrahydrofuran, benzene, toluene and xylene. It is insoluble in n-hexane and hydroxyl-group containing solvents such as methanol and ethanol.

3.2. Characterization of polymers

The FT-IR spectrum of poly(DMOPM) shows a peak at 3103 and 3075 cm^{-1} due to the C–H stretching of the aromatic ring. The peaks at 3000, 2942 and 2839 cm^{-1} are attributed to the unsymmetrical and symmetrical C–H stretching of methylene and methyl groups. The ester carbonyl stretching is observed at 1751 cm^{-1}.