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Studies on photocrosslinkable copolymers of 4-methacryloyloxyphenyl-3′,4′-dimethoxystyryl ketone and methyl methacrylate

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Abstract

Copolymers with various contents of 4-methacryloyloxyphenyl-3′,4′-dimethoxystyryl ketone (MPDSK) and methyl methacrylate (MMA) were prepared in methyl ethyl ketone solution using benzoyl peroxide as a free radical initiator at 70 °C. Characterization of the resulting polymers was done by UV, FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopic techniques. The copolymer compositions were determined by ^{1}H NMR analysis. The monomer reactivity ratios were calculated using linearisation methods such as Finemann–Ross ($r_1 = 0.4283$ and $r_2 = 0.3050$), Kelen–Tudos ($r_1 = 0.4264$ and $r_2 = 0.2606$), and extended Kelen–Tudos ($r_1 = 0.4022$ and $r_2 = 0.2704$) methods as well as by a non-linear error-in-variables model (EVM) method using the computer program RREVM ($r_1 = 0.4066$ and $r_2 = 0.2802$). The molecular weights ($\overline{M}_w$ and $\overline{M}_n$) and the polydispersity index of the copolymers were determined by gel permeation chromatography. The thermal stability of the copolymers increases with increase in concentration of MPDSK. Glass transition temperatures were determined by differential scanning calorimeter under nitrogen atmosphere. The photoreactivity of the copolymers having pendant chalcone moieties was studied in chloroform solution.

Keywords: 4-Methacryloyloxyphenyl-3′,4′-dimethoxystyryl ketone; Methyl methacrylate; Photocrosslinkable polymers; Reactivity ratios; ^{1}H NMR and ^{13}C NMR spectra

1. Introduction

Photoreactive materials have recently gained remarkable interest since the photochemical reaction in organic materials can induce many changes in physicochemical properties such as solubility, absorbability of light, flexibility and elasticity [1–4]. Polymers containing unsaturated aromatic acid or ester units, for example the cinnamic acid and cinnamic ester derivatives, were used for the study of phototransformation phenomena that occur under UV irradiation [5,6]. Photosensitive polymers find applications in fields such as integrated circuit technology, energy exchange materials [7], photorecorders [8], photocurable coatings [9], advanced microelectronics [10], photolithography [11] and liquid

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crystalline displays [12]. Examples of photosensitive polymers containing chalcone units in the side chains include β-vinyloxyethyl cinnamates [13], poly(vinyl-4-methoxy cinnamate) [14], poly(vinylcinnamoxy acetate) [15], poly(vinyl cinnamate) [16], poly(4-vinylphenyl cyanate) [17], poly[4-(2-hydroxy ethyloxy)-*N*-(5-nitro-2-thienylmethylene)]aniline [18], and poly(2-(*N*-phthalimido)-2-methyl propyl acrylate) [19]. Apart from these a variety of photosensitive polymers containing pendant cinnamoyl groups such as vinylphenyl cinnamate, isopropenylphenyl-β-styryl acrylate, and copolymers of 2-cinnamoyloxyethyl methacrylate [20] have been reported.

The chemical composition of the copolymers depends on the degree of incorporation of the comonomers, i.e., on the relative reactivity between them. Monomer reactivity ratios are very important quantitative values to predict the copolymer composition for any starting feed and to understand the kinetic and mechanistic aspects of copolymerization. In the past few decades, ^{1}H NMR spectroscopic analysis has been established as a powerful tool for the determination of tacticity and sequence distribution as well as for the estimation of copolymer composition because of its simplicity, rapidity and sensitivity [21–24]. The accurate estimation of copolymer composition and determination of monomer reactivity ratios is significant for tailor-made copolymers with required physical and chemical properties and in evaluating the specific end application of the copolymers. The main aim in commercial copolymerization is to achieve a desirable product composition. Knowledge about the monomer reactivity ratios of the comonomers would help in achieving this. The present work is aimed to develop new photoresist materials based on the copolymers of 4-methacryloyloxyphenyl-3′,4′-dimethoxystyryl ketone with methyl methacrylate. In this article, we report the synthesis, characterization, thermal stability, and photocrosslinking properties of copolymers of 4-methacryloyloxyphenyl-3′,4′-dimethoxystyryl ketone (MPDSK) with methyl methacrylate (MMA) and determination of monomer reactivity ratios for the comonomers MPDSK and MMA.

2. Experimental

2.1. Materials

The methacrylate monomer, 4-methacryloyloxyphenyl-3′,4′-dimethoxystyryl ketone was prepared by reacting 4-(3′,4′-dimethoxycinnamoyl)phenol with methacryloyl chloride in the presence of triethyl amine in MEK following the procedure of Balaji and Nanjudan [25]. Benzoyl peroxide (BPO) was recrystallized from a 1:1 mixture of chloroform and methanol. Methyl methacrylate was purified by washing with 5% NaOH solution, followed by distilled water, dried over anhydrous sodium sulfate and distilled twice under reduced pressure. All other solvents were distilled before use.

2.2. Copolymerization

Copolymers of MPDSK and MMA of six different compositions were prepared in MEK solution using benzoyl peroxide as a free radical initiator at 70 °C. Appropriate quantities of MPDSK and MMA with MEK and BPO were placed in a standard reaction tube and the mixture was flushed with oxygen-free nitrogen for 15 min. The tube was then tightly sealed and immersed in a thermostatic oil bath at 70 °C. After the required time, the copolymers were precipitated in methanol, and purified by reprecipitation with methanol from a solution of the polymer in MEK. They were then filtered and dried in a vacuum oven at 40 °C for 24 h.

2.3. Measurements

FT-IR spectra were recorded on a Hitachi 270-50 spectrophotometer using KBr pellets for solid samples. High-resolution ^{1}H NMR spectra were run on Bruker 270 MHz spectrometer and the spectra were recorded at room temperature as 15–20% (w/v) solutions in $CDCl_3$. The same instrument was used to record ^{13}C NMR spectra in DMSO-d_6 at room temperature using tetra methyl silane (TMS) as an internal standard. Ultra-violet spectra of the polymers were recorded with a Hitachi UV-2000 spectrophotometer. The number-average molecular weight ($\overline{M}_n$) and weight-average molecular weight ($\overline{M}_w$) were determined by a Waters 501 gel permeation chromatograph equipped with three ultra styragel columns and a differential refractive index detector. Tetrahydrofuran was used as the eluent and polystyrene standards were employed for calibration. Thermogravimetric analysis (TGA) curves were recorded with a Mettler TA 3000 thermal analyzer in air at a heating rate of 15 °C/min. The glass transition temperature (T_g) was determined using a Perkin–Elmer DSC d7 differential scanning calorimeter (DSC) at a heating rate of 10 °C/min in nitrogen atmosphere.

2.4. Photoreactivity measurement

A low-pressure mercury lamp (Heber Scientific photo reactor-UV, 6 W, 254 nm) was used as the UV source for the irradiation of the polymers in solution. The polymer dissolved in chloroform was kept at a distance of 10 cm from the UV lamp for different time intervals of irradiation. The UV spectra of the polymer in solution were recorded immediately after each exposure, and the rate of disappearance of the >C=C< double bond