



Synthesis and characterization of new photoresponsive acrylamide polymers having pendant chalcone moieties

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Abstract

New acrylamide monomers, 4-acrylamidophenyl-2',3'-benzostyryl ketone (APBSK) and 4-acrylamidophenyl-4'-*N,N'*-dimethylstyryl ketone (APDSK) having a free-radical polymerizable group and a photocrosslinkable functional group, were synthesized by reacting the corresponding aminochalcones with acryloyl chloride in the presence of triethyl amine. The monomers were polymerized in methyl ethyl ketone at 70 °C using benzoyl peroxide as the initiator. The resulting polymers were characterized by UV, IR, ¹H NMR and ¹³C NMR spectroscopy. The polymers were found to be soluble in several polar aprotic solvents and in chlorinated solvents but insoluble in aliphatic and aromatic hydrocarbons and in alcohols. The molecular weight data of the polymers as obtained from gel permeation chromatography suggests a higher tendency for chain termination by dimerization than disproportionation. The glass transition temperature of the polymers was determined by differential scanning calorimetry. Thermogravimetric analysis of the polymers carried out in air reveals that the polymers possess good thermal and thermo-oxidative stability required of a negative photoresist. The photosensitivity of the polymer was investigated in various solvents in the presence and absence of triplet photosensitizers. The effect of the different solvents and concentration on the rate of photocrosslinking of the polymers were also examined for using the polymers as negative photoresist materials.

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1. Introduction

Photosensitive polymers with photocrosslinkable groups have gained a considerable interest in

recent years owing to a wide variety of applications in the field of macro- and microlithography [1,2], printing [3], liquid crystalline display [4] nonlinear optical materials [5,6], holographic head-up-display [7], integrated circuit technology [8], photocurable coatings [9], photoconductors [10], energy exchange materials [11], etc. UV

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radiation curing has been revealed as a powerful tool to crosslink rapidly the heat sensitive polymers and modifies, selectively in the illuminated areas, their physico-chemical characteristics. Photo-tuneable technology have found major openings in various industrial applications where its distinct advantages such as fast cure, selective cure and ambient temperature have allowed this environmental friendly technology to outclass more conventional processing techniques. Among the various photocrosslinkable groups, α , β -unsaturated carbonyl unit has attracted particular attention due to its excellent photoreactivity at UV absorption wavelength [12–16]. Crosslinking with ultraviolet light is an excellent method for obtaining articles with thick cross-sections, with or without reinforcement, without significant heat buildup in the interior, which could damage the plastic [17]. Polymers with chalcone or cinnamoyl group either in the backbone [18] or side chain undergo crosslinking through $[2\pi + 2\pi]$ cycloaddition of the carbon–carbon double bond upon irradiation with UV light [19–21] and such polymers are regarded as negative-type photoresists. These polymers with the properties of high photosensitivity, the ability to form films, good solubility before irradiation, resistance towards solvents, plasmas and etching agents after crosslinking and good thermal stability are very important for commercial photoresist applications.

Several polymers with pendant photofunctional groups have been reported, e.g., poly(vinyl cinnamate) [22], poly(vinyl-4-methoxycinnamate) [23], cinnamoyl derivative of poly(2-hydroxyethyl methacrylate) [24], poly(4-cinnamoyl phenyl methacrylate) [25], phosphazene based cinnamate photopolymers [26,27], condensation product of poly(vinyl acetophenone and benzaldehyde) [28], cinnamoylated cellulose [29], poly(vinyl ethyl cinnamate) [30], poly(vinyl ethyl carbonyl chalcone) [31], cinnamoylated product of partially hydrolyzed poly(vinyl acetate) [32], poly(4-Acryloyloxy/methacryloyloxy phenyl substituted styryl ketones [33,34], poly(substituted cinnamoyl phenyl acrylate/methacrylate) [35,36] etc.

As far as we know, no reports have been observed in the literature about the synthesis of

photocrosslinkable acrylamide polymers bearing chalcone as a pendant group. In this paper, we report the synthesis, characterization, thermal stability and photocrosslinking properties of acrylamide based photocrosslinkable polymers, poly(4-acrylamidophenyl-2',3'-benzostyryl ketone) [poly(APBSK)] and poly(4-acrylamido phenyl-4'-*N,N'*-dimethylstyryl ketone)[poly(APDSK)]. The effect of different solvents and concentration of polymers on the rate of photocrosslinking is also assessed for using the polymers as negative photoresist materials. One of the important advantages of these polymers is they are highly photosensitive and they do not require photosensitizers to increase their photo activity.

2. Experimental

2.1. Materials

4-Aminoacetophenone (SRL), 1-naphthaldehyde (Lancaster) and 4-*N,N'*-dimethylaminobenzaldehyde (Merck) were used as received. Benzoyl peroxide (BPO) was recrystallized from a 1:1 mixture of methanol and chloroform. Acryloyl chloride was prepared by reacting acrylic acid with benzoyl chloride following the procedure of Stampel et al. [37]. All the other solvents were distilled before use.

2.2. Preparations

2.2.1. Synthesis of 4-(2',3'-benzocinnamoyl) aniline

4-Aminoacetophenone (7 g, 0.0517 mol) in 60 ml of ethanol and a solution of sodium hydroxide (2 g) in distilled water (30 ml) were placed in a three necked flask equipped with a mechanical stirrer, a thermometer and a dropping funnel and were cooled in an ice bath. 1-Naphthaldehyde (8 g, 0.0517 mol) dissolved in 50 ml of ethanol was added to it dropwise with constant stirring such that the temperature was not exceeded 20 °C. After stirring the reaction mixture at room temperature for 24 h, the product formed was filtered, washed thoroughly first with ice cold water and finally with cold alcohol. After drying the product it was recrystallized from ethyl acetate to get pure

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