



Photochromism of photopolymerized novel copolymers having spirooxazine moiety groups

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Abstract

A novel class of photochromic copolymer based on spironaphthoxazine (SO) moieties was smoothly prepared through the copolymerization of methyl methacrylate (MMA), butyl acrylate (BA) and SO-based monomer by photopolymerization. Polymerization efficiency was studied by measuring the content of SO in eluents, which decreased with increasing mass ratio of SO in precursor monomer. The incorporated SO moieties endow the copolymers with remarkable photochromic ability. The novelty of this study is that unlike conventional physically blending photochromic polymer, SO moieties were chemically bonded with polymer chain, which is an effective way to prevent the SO from migration, thus increasing the stability and reliability during the long-term application. Moreover, the copolymerization was prepared through UV polymerization in the absence of organic solvent, which is environmentally friendly. Polymer chain flexibility can be well tuned by changing the mass ratio of BA. To make the copolymer more flexible, plasticizer of dibutyl phthalate (DBP) was also introduced. The photochromic ability of the as-prepared films was enhanced with increase in flexibility of polymer chain, which achieved the optimum state when the mass ratios of plasticizer DBP (dibutyl phthalate) and precursor BA (butyl methacrylate) were 20% and 50%, respectively. The thermal stability and tensile strength of the products were characterized by thermogravimetric analysis and electronic universal testing machine, which revealed that these copolymers could be applied as photochromic materials.

Keywords Photochromic polymer · Spirooxazine · Photopolymerization · Polymethyl methacrylate · Solvent-free

Introduction

Photochromic polymers (PCPs), which can reversibly change colors under UV irradiation, have enabled various sensing and displaying applications as decorative coatings, smart windows, chemical sensing and optical data-storage devices [1–3]. Generally, PCPs are composed of photochromic units and polymeric matrix. Typical examples of photochromic units include azobenzene [4–6], diarylethene [7, 8], phenoxynaphthacenequinone [9], spiropyran [10–12] and spirooxazine [13, 14]. Among them, spirooxazines (SO) are of particular interest due to their

favorable properties of good photostability, outstanding fatigue resistance, excellent chromogenic stability and high photoresponse rate [13, 15, 16]. The photochromism of SO results from the reversible isomerization reaction between merocyanine form (non-planar structure) and spirocyclic form (planar structure), which is due to reversible rupture (under UV light) and re-adjusted (without UV irradiation) of C–O bond in SO structure (as illustrated in Scheme 1). On the other hand, polymeric matrices are essential components for the fabrication of PCPs, and exhibit an important influence on the isomerization of SO molecules. Normally, polyurethanes, epoxy resins, polystyrenes and acrylonitrile–butadiene rubber have been used as polymer matrices for PCPs. For a polymer to be as useful polymeric matrix for PCPs, it is better to meet criteria such as good mechanical properties, high transparency, outstanding thermal stability and environmentally friendly mass production. Moreover, to achieve the applicable photochromism, polymer matrix with lower glass transition temperature (T_g) is preferred. Previous works

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