

Synthesis, thermal and optical properties of crosslinked poly(isobornyl methacrylate-co-butyl acrylate) copolymer films



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ABSTRACT

Novel crosslinked poly(IBOMA-co-BA) copolymers were prepared by free-radical copolymerization from isobornyl methacrylate (IBOMA) and butyl acrylate (BA), using 4,4'-isopropylidenediphenol dimethacrylate (BD) as crosslinking agent and 2,2'-azobisisobutyronitrile (AIBN) as thermal initiator. The chemical structures, physical and optical properties of the resultant copolymers were characterized by FTIR, ¹H NMR, differential scanning calorimetry, thermogravimetry analysis, refractive index and birefringence measurements. It was found that the crosslinking modification could effectively improve the resistance to organic solvents, and significantly increase the glass transition temperatures and thermal stability of the copolymers. More importantly, the transparent copolymer films with three-dimensional network structures exhibited very low birefringence. In addition, with the incremental increase of the BD content in copolymers from 15 wt% to 60 wt%, the refractive indices of films could be tunable over a range of 1.475–1.546. The excellent chemical resistance, thermal and optical properties endow this series of polymer materials with promising application in light-waveguide device field.

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1. Introduction

Poly(meth)acrylates have been widely employed in optical devices, optical eyewear, optoelectronic devices and microelectronics fields [1]. Compared to inorganic materials, organic poly(meth)acrylates possess numerous merits including ease of process, light weight, flexibility, low cost, excellent transparency, capability of transmitting large quantities of light, and good compatibility with various materials [2–4]. The above characteristics make them suitable for the fabrication of light-waveguide devices. Among poly(meth)acrylates, poly(isobornyl methacrylate) [poly(IBOMA)] and its copolymers are receiving great attention recently because of their unique chemical structure. The monomer IBOMA contains a bulky bicyclic group. After polymerization, relative to common poly(meth)acrylates, the rigid and hydrophobic side group gives rise to poly(IBOMA) large hardness, low water absorption, high glass transition temperature and high dimension stability [5–13]. Up to now, however, the survey of literature reveals that very few studies have been reported on optical properties of poly(IBOMA) and its copolymers.

For the design and synthesis of new optical polymer materials, it is desirable that the refractive index can be continuously tunable within a wide range. Thus, the selection of materials for the core

and cladding layers of light-waveguide device will be convenient [3]. Moreover, utilization the same kind of polymers for core and cladding layers is conducive to achieve good interface compatibility, and the thermal expansion coefficients between two layers are more matchable [14]. Usually, the refractive index of a material is closely related to its free volume, polarizability, temperature, and water absorption rate [15]. The dense packing of polymer chains is advantageous for a high refractive index [16]. In addition, the introduction of π - π^* conjugated structure with large molecular polarizability into polymer backbone can effectively increase refractive index of a polymer material as well [15,17].

On the other hand, as optical materials, excellent resistance to chemical corrosion and moisture penetration, high glass transition temperature, good thermal stability are extremely important. In this respect, crosslinked polymers with three-dimensional network structure have significant advantages over linear polymers. Birefringence, defined as the difference between the refractive indexes measured in TE mode (transverse electric mode) and in TM mode (transverse magnetic mode), is caused by the optical anisotropy of the polymer due to the orientation of chain segments [18,19]. The previous study has shown that, after crosslinking modification, the birefringence value of polymer films can be remarkably reduced [4].

Based on the above considerations, in this paper, at first, aromatic 4,4'-isopropylidenediphenol dimethacrylate (BD) was synthesized, which was then utilized as a crosslinker to

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copolymerize with isobornyl methacrylate (IBOMA) and butyl acrylate (BA) to produce crosslinked copolymer films by radical polymerization. Small amounts of BA were incorporated into polymer chain in order to improve the flexibility, while the BD content in the system varied from 15 wt% to 60 wt% to systematically adjust the crosslinking densities and refractive indices of polymer films. This paper investigated the synthesis and characterization of crosslinked poly(IBOMA-co-BA) copolymers as well as the influence of BD content on chemical resistance, thermal and optical properties of polymer films.

2. Experimental

2.1. Materials

Bisphenol A, methacrylic acid, isobornyl methacrylate, butyl acrylate, thionyl chloride and 2,2'-azobisisobutyronitrile (AIBN), tetrabutyl ammonium bromide (TBAB) were purchased from Shanghai Regent Corporation Ltd. Isobornyl methacrylate and butyl acrylate were purified by successively washing with 5% aqueous NaOH and deionized water, and then, after drying with anhydrous MgSO₄, they were distilled under reduced pressure over CuBr. AIBN was recrystallized from methanol prior to use. Methacryloyl chloride was prepared by reaction from methacrylic acid and thionyl chloride according to the procedure described in literature [20]. Other reagents were used as received.

2.2. Measurements

Fourier transform infrared spectra (FTIR) were recorded using a Nicolet 20XB FTIR spectrophotometer in the 400–4000 cm⁻¹ region with KBr flake.

¹H NMR was carried out on an INOVA-400 NMR spectrometer (Varian) using CDCl₃ as solvents, tetramethylsilane (TMS) as an internal standard.

DSC curves were measured by a NETZCH DSC 204 thermal analyzer using N₂ as a purge gas (20 ml/min) at a heating rate of 10 °C/min. About 5–10 mg sample was put into the aluminum pan for DSC measurement.

Thermogravimetric analyses (TGA) were run on NETZSCH TG209C under nitrogen atmosphere and conducted with a heating rate of 10 °C/min. The temperature range was from room temperature to 800 °C. In order to eliminate the effect of possible adsorption of moisture from atmosphere, all the samples were dried at 80 °C under vacuum for 6 h before measurements.

The refractive indices n_{TE} and n_{TM} at the transverse electric (TE) and transverse magnetic (TM) modes of the films were measured by using a Sairon SPA-4000 prism coupler with a gadolinium gallium garnet (GGG) prism at room temperature at the wavelengths of 1310 nm and 1550 nm, respectively, with the accuracy of 0.001 and the resolution of ±0.0005. The birefringences (Δn) were calculated as the difference between n_{TE} and n_{TM} . For each sample, at least three pieces of films were measured and their values were averaged.

2.3. Synthesis of 4,4'-isopropylidenediphenol dimethacrylate

4,4'-Isopropylidenediphenol dimethacrylate (BD) was synthesized through a two-phase reaction according to Ref. [21] with some modifications. At around 5 °C, bisphenol-A (3 g, 13.16 mmol), TBAB (0.08 g), potassium hydroxide (2.37 g, 42.4 mmol), deionized water (25 mL) and dichloromethane (15 mL) were added into the three-neck flask equipped with thermometer, mechanical stirring and dropping funnel. Then, the newly prepared methacryloyl chloride (2.6 mL, 27.0 mmol) was slowly added dropwise. After stirring

for 1 h, the oil phase was collected and washed with deionized water until the solution became neutral. The solution was dried over MgSO₄ and filtrated. The filtrate was evaporated on a rotary evaporator to remove the solvent. Then, the crude product was further purified through silica gel column chromatography to afford a white solid. Yield 95%; mp 61–62 °C. FTIR (cm⁻¹): 3035 (H–Ar), 2969, 2923 (–CH₃), 1731 (C=O), 1635 (C=C), 1604, 1504 (C=C, Ar), 1212, 1171 (C–O–C). ¹H NMR (400 MHz, CDCl₃/TMS, ppm): 7.01–7.26 (q, 8H, Ar–H), 6.33 (2H, =C–H), 5.74 (2H, =C–H), 2.05 (6H, =C–CH₃), 1.68 (6H, C–CH₃).

2.4. Preparation of crosslinked copolymer films

The crosslinked copolymer films were prepared on silicon wafers. Prior to use, wafers were treated with a piranha solution (4:1 mixture of H₂SO₄ and H₂O₂) at 80 °C for 1 h, rinsed with deionized water for 30 min, and then blew dried with nitrogen stream.

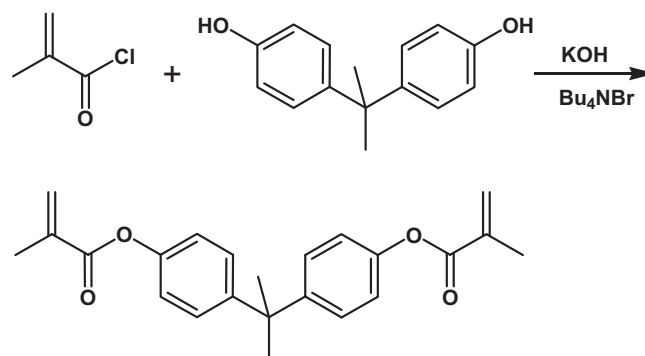
The copolymer films with different contents of BD were prepared in a similar procedure, so only the preparation for the polymer with 15 wt% BD is described here as an example. 1.75 g IBOMA, 0.75 g BA, 0.44 g BD and 0.03 g AIBN were dissolved in 6 mL of 1,1,2-trichloroethane. The solution was filtered through a 0.22-mm Teflon filter, and then cast on a clean silicon wafer. The film was cured under a nitrogen atmosphere at 65 °C for 2 h, 90 °C for 2 h, and finally 120 °C for 2 h.

3. Results and discussion

3.1. Synthesis and characterization of crosslinked poly(IBOMA-co-BA) films

The crosslinker (BD) was synthesized through a two-phase reaction according to the synthetic route illustrated in Scheme 1. The strong alkali was added in aqueous phase to improve the reactive activity of phenolic hydroxyl groups. To ensure a complete reaction of hydroxyls, slightly excess methacryloyl chloride was charged in the system. The reaction was carried out at a low temperature of around 5 °C in order to reduce the possible side reactions. The crude product was purified by column chromatography.

The chemical structure of BD was confirmed by FTIR and ¹H NMR spectra. As shown in Fig. 1, the characteristic absorptions at 1731 cm⁻¹ and 1171–1212 cm⁻¹ are due to C=O and C–O–C bonds of ester group, respectively. The band at 1635 cm⁻¹ is assigned to C=C double bond of methacrylate group. The band at 1504 cm⁻¹ is attributed to aromatic benzene ring of BD. In the ¹H NMR spectrum of BD (Fig. 2), the signals at 7.01–7.26 ppm are attributed to the aromatic protons of BD, whereas the peaks at around 5.74 and 6.33 ppm are assigned to the protons of C=C



Scheme 1. Synthesis of 4,4'-isopropylidenediphenol dimethacrylate (BD).

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