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Acrylic ABA triblock copolymer bearing pendant reactive bicycloalkenyl functionality via ATRP and tuning its properties using thiol-ene chemistry

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A B S T R A C T

This investigation reports the preparation of tailor-made ABA triblock copolymers (BCP) of 2-ethylhexyl acrylate (PEHA) and dicyclopentenyloxyethyl methacrylate (PDCPMA) bearing pendant reactive cycloalkenyl functionality via atom transfer radical polymerization (ATRP) and thiol-ene modification of the pendant reactive bicycloalkenyl functionality. The chemical structure and molar composition of the polymers were determined by ^{1}H NMR spectroscopy and molecular weights of the polymers were determined by gel permeation chromatography. AFM as well as DSC analysis showed nanophase-separated morphology in the block copolymers. The pendant reactive bicycloalkenyl group of PDCPMA in the BCPs was successfully modified by thiol-ene reaction and the mechanical properties of the modified BCPs were studied. The thiol modified BCP showed much greater adhesion strength compared to pristine BCP as determined by lap shear test using a UTM. Hardness of the BCP film and UV-cured thiolated BCP film was studied and compared by using a nanoindenter.

1. Introduction

Block copolymers (BCP) of acrylates and methacrylates are important polymeric materials, because of their interesting properties, like improved optical properties, excellent resistance to oxidation and improved mechanical properties [1–5]. These properties can be tuned by unique combination of a hard block (methacrylate) with a soft block (acrylate) [2,6–9]. They have applications in contact lens, surfactants and emulsifiers, compatibilizing agents in polymer blends, biomedical applications and in thermoplastic elastomers (TPE) [10–15]. Acrylic polymers are also used as adhesive materials as well as important ingredients in paints, coatings, pharmaceuticals and cosmetics [16–18].

It is well known that living polymerization technique is the most efficient tool for the synthesis of well-defined BCPs with narrow molecular weight distribution (MWD). Ionic polymerizations need very stringent reaction conditions and complex experimental set up. Small amount of adventitious impurities present in the solvent, initiator, monomer and side reactions of the anionic species often affect the ionic polymerizations [19–21]. During the last couple of decades, the controlled radical polymerizations (CRP) have been important synthetic tools to prepare polymers with controlled molecular weight and well-defined architecture [22,23]. Among different types of CRP, atom transfer radical polymerization (ATRP) is very versatile and is suitable method for the synthesis of different tailor-made polymers with complex architectures like block copolymers, star polymers, hyperbranched polymers with controlled molecular weights and low polydispersities [8,22–26]. Polymers of dicyclopentenyloxyethyl methacrylate (DCPMA) are interesting materials due to the presence of reactive double bond in the pendant bicyclic moiety [27,28]. This reactive double bond can be used for post-polymerization modification like thiol-ene reaction. Recently we have reported the preparation of poly(dicyclopentenyloxyethyl methacrylate) via ATRP. However, there is no report on the preparation of triblock copolymer of DCPMA via ATRP and subsequently the thiol-ene modification of this kind of BCP. There are several reports of acrylic block copolymers comprising of conventional (meth)crylates. However, it is difficult to prepare well-defined block copolymers of DCPMA, because DCPMA undergoes several side reactions leading to gel formation during the course of polymerization reaction [27,28].

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The objective of this present work is to prepare ABA triblock copolymers (PDCPMA-*b*-PEHA-*b*-PDCPMA) bearing reactive alkenyl functionality with controlled molecular weight via ATRP and to modify the BCP via thiol-ene chemistry to tune its mechanical properties. Here poly(2-ethylhexyl acrylate) (PEHA), which has very low T_g and good film formation properties was used as a middle block and poly(dicyclopentenyloxyethyl methacrylate) (PDCPMA) having the pendant cycloalkenyl functionality was used as the side block in the triblock BCP. The ABA block copolymers were modified by the thiol-ene reaction and then they were explored as an adhesive material in the metal to metal bonding. The block copolymers were characterized by ^{1}H NMR, GPC analysis and AFM analysis. The adhesive strength was analyzed by lap shear test using a universal testing machine (UTM). Nanoindentation experiment shows that the UV-cured thiolated BCPs have higher surface hardness than that of pristine BCP.

2. Experimental

2.1. Materials

The monomers, dicyclopentenyloxyethyl methacrylate (DCPMA) (99%, Aldrich), and 2-ethylhexyl acrylate (EHA) (98%, Aldrich) were purified by passing through basic alumina column followed by vacuum distillation, and then were stored in a refrigerator. CuBr (98%, Aldrich) was purified by washing with glacial acetic acid, followed by diethyl ether, and then was dried under vacuum. Triethyl amine (Merck, India) was distilled before use. Ethylene glycol (99.8%, Aldrich), 2-bromoisobutyryl bromide (97%, Aldrich), N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA) (99%, Aldrich), 2-mercaptoacetic acid (Merck), 2-mercaptoethanol (99%, SRL Pvt., Ltd.), benzyl mercaptan (97%, Aldrich), trimethylolpropane tris-(3-mercaptopropionate) (TRIS) (98%, Aldrich), 2,2′-azobisisobutyronitrile (AIBN) (98%, ACROS Chemical) and Irgacure 184 (Ciba Speciality Chemicals) were used as received. Solvents were distilled prior to use.

2.2. Characterization

2.2.1. Gel permeation chromatography (GPC)

The molecular weight and polydispersity index of the polymers were measured by gel permeation chromatography (GPC) at ambient temperature using VISCOTEK-Malvern, GPC instrument equipped with two ViscoGel mix bed columns (17360-GMHHRM) connected in series with a refractive index detector model, VE 3580 RI detector. THF was used as an eluent at a flow rate of 1.0 mL/min and poly(methyl methacrylate) of narrow polydispersity was used as calibration standard. For collecting the GPC data OmniSEC 4.2 software was used.

2.2.2. Nuclear magnetic resonance spectroscopy (NMR)

^{1}H NMR spectra of the polymers were recorded at 400-MHz Bruker NMR spectrometer with tetramethyl silane (TMS) as an internal reference. $CDCl_3$ was used as the solvent for all NMR spectra unless otherwise stated.

2.2.3. Atomic force microscopy (AFM)

Silicon wafer of [100] orientation was cut into 2 cm × 1 cm dimension and ultrasonicated in dichloromethane for 20 min. Then the silicon wafers were treated with 1:1:1 v/v/v mixture of 29% H_2O_2, 30% ammonium hydroxide and Millipore water at 65 °C for 90 min. Afterwards the silicon wafers were thoroughly rinsed with Millipore water until pH 7 followed by drying under nitrogen flow.

1 wt% solution of block copolymer prepared in THF at room temperature. Thin films of block copolymer (PDCPMA-*b*-PEHA-*b*-PDCPMA) were prepared on silicon wafers by spin coating followed by drying under hood to get rid of traces of solvent. The block copolymer films casted on silicon wafer were further annealed in toluene for improvement of morphology in nanoscale. For solvent annealing the films were exposed to toluene for 10 min in the presence of saturated toluene vapour. The phase separation of block copolymer films before and after solvent annealing was investigated by AFM analysis. AFM was carried out in tapping mode using Dimension ICON (Bruker-Nano, USA) operated at room temperature in air. The images were digitally sampled at the maximum pixels (512) in each direction and image analysis was done using the Nanoscope Analysis software.

2.2.4. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) analysis was carried out on a TA (DSC Q100 V8.1 Build 251) instrument at a temperature range of -90 °C to 70 °C at a heating rate of 10 °C/min under nitrogen atmosphere. The second heating cycle curve was used to determine the T_g of the polymers.

2.2.5. Lap shear test

Lap shear test was carried out in Hounsfield H10KS universal testing machine. For adhesion test aluminium plates were used. The plates were cleaned by rubbing the surface using emery paper and then the solutions of both modified and unmodified triblock copolymer were applied over an area of 1 inch at one end of the polished surface of every plate to form a uniform layer of adhesive. Then the adhesive coated surface of the specimens was joined face to face and was kept under constant weight of 5 kg for 5 days to press the specimens. The shear strength of the polymeric adhesives was measured at ambient condition at a cross-head speed of 50 mm/min.

2.2.6. UV curing

UV radiation was carried out using an Ultraviolet Medium Pressure Quartz Lamp having wavelength of around 250–350 nm in a UV chamber (Model No. ACS 21-12 Cabinet purchased from Advanced Curing System, Bangalore, India). For UV-curing experiment, films were cast from a THF solution containing the triblock copolymer, trimethylolpropane tris-(3-mercaptopropionate) and the Irgacure 184 photoinitiator on a glass plate. Samples were exposed to UV radiation in the ACS UV curing chamber for 1 min at ambient temperature.

2.2.7. Nanoindentation experiment

Surface hardness of the BCP and UV-cured films was measured with a TI 950 TriboIndenter, Hysitron Inc., USA. The hardness measurements were performed with a constant load of 40 μN. The nanoindentation experiments were carried out at room temperature.

2.3. Synthesis of bifunctional initiator 1,2-bis(bromoisobutyryloxy) ethane (BBiBE)

The bifunctional initiator, 1,2-bis(bromoisobutyryloxy)ethane (BBiBE) was prepared by the esterification reaction of ethylene glycol and 2-bromoisobutyryl bromide in presence of triethyl amine. In a 100 mL round bottom flask ethylene glycol (1 g, 1.6×10^{-2} mol), triethyl amine (3.25 g, 3.22×10^{-2} mol), and 25 mL of dichloromethane were placed along with a magnetic bar and were kept it in an ice-bath. To this, 2-bromoisobutyryl bromide (7.4 g, 3.22×10^{-2} mol) was added drop wise. The reaction was continued at this temperature for 1 h and after that the ice-bath was removed. This mixture was stirred overnight at room temperature. Then the reaction mixture was washed and extracted several times with distilled water and dichloromethane respectively. Then the organic layer was washed with $NaHCO_3$ and brine