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Synthesis of UV-curable acrylate polymer containing sulfonic groups for anti-fog coatings

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ABSTRACT

A series of UV curable hydrophilic acrylate polymers containing sulfonic acid group was prepared via free radical copolymerization using 2-acrylamido-2-methyl propane sulfonic acid (AMPS) as hydrophilic monomer, which were used as prepolymers for anti-fog coatings. The expected structures were confirmed by FT-IR, ^{1}H NMR and gel permeation chromatography (GPC). These UV-curable acrylate polymers were then mixed with reactive diluents and photoinitiator to form coating formulas. Various substrates were coated with these formulas and cured under UV exposure to obtain transparent coatings with good adhesion and hardness. The anti-fog properties of UV-cured coating were measured by contact angle test and anti-fog test. The results showed that the AMPS content in prepolymer had a great influence on the anti-fog properties of UV-cured coating. The formula was optimized and the corresponding UV-curing anti-fog coating was manufactured. The test results indicated that the coatings showed good mechanical properties, great optical transparency and excellent anti-fog performance.

1. Introduction

Water vapor can condense on solid surface at a certain temperature or humidity, and water on surface forms little droplets if the solid surface has a very high surface energy. Therefore the light is refracted and scattered by water droplets and the transparent materials turn hazy, which causes fogging problems. Many optical devices are suffering from fogging problems, such as eyeglasses, mirrors, windshields and many other devices in special fields [1–4]. There are two efficient ways to solve the problem. One is to heat the device to make water vapor non-condensing, and the other is to provide the solid surface with wetting characteristics such as hydrophilicity [5] or even super hydrophilicity [6]. Although the former method is efficient, the cost of energy limits its wide application.

Hydrophilic surfaces that have contact angles with water of less than 40° are often explored as anti-fog coatings. The main reason is that condensing water droplets on this type of surface can rapidly spread into a uniform and non-light-scattering water film [7,8]. In this case, although condensation still occurs, the surface remains optically clear. The key to this approach is the use of materials which can strongly interact with water molecules and/or have a high capacity to absorb water. Hydrophilic polymeric systems containing hydroxyl groups (—OH), amino group (—NH_2), carboxyl group (—COOH) or sulfonic group (—SO_3H) are often utilized in anti-fog formulas [9,10]. However, the preparation of optical quality thin-film coatings with these hydrophilic functionalities exhibiting both good coating characteristics and mechanical durability is still a great challenge.

Herein, a new coating system with good anti-fog properties and mechanical properties was presented. This new coating system was based on a UV-curable hydrophilic polymer which was prepared via free radical copolymerization with 2-acrylamido-2-methyl propane sulfonic acid (AMPS) as hydrophilic monomer. After UV-curing, the resultant coating exhibited good anti-fog properties as well as good mechanical properties.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA), 2-ethylhexyl acrylate (EHA), 2-hydroxyethyl methacrylate (HEMA), 2-acrylamido-2-methyl propane sulfonic acid (AMPS), isophorone diisocyanate (IPDI), 2,2′-azobisisobutyronitrile (AIBN), potassium hydroxide (KOH), methyl alcohol (MeOH), dibutyltin dilaurate (DBTDL), 4-methoxyphenol (MEHQ), acetic ether (EAc), N,N-dimethylformamide (DMF) were all purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

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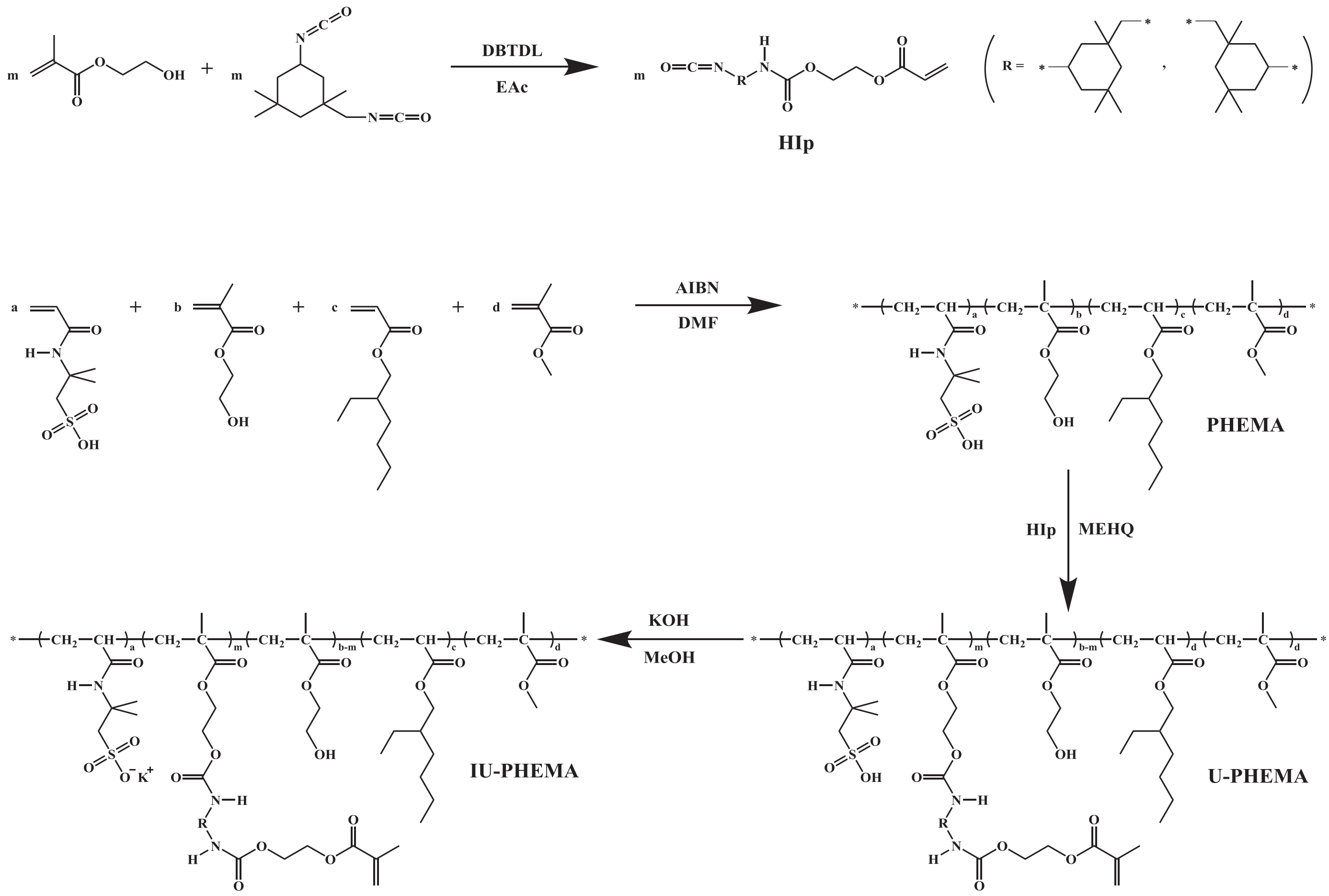

Scheme 1. The synthetic route of IU-PHEMA.

1-Hydroxycyclohexyl phenyl ketone (HCPK), 1,6-hexanediol diacrylate (HDDA), ethoxylated trimethylolpropane triacrylate (EOTMPTA), trifunctional acid ester (CD9051), phosphate (w190) were all supplied by Jiangsu Kuangxin Photosensitivity New-material Stock Co., Ltd. (Wuxi, China).

2.2. Synthesis of prepolymer

An isocyanate-containing unsaturated monomer named as HIp was prepared via nucleophilic addition of IPDI and HEMA. The molar ratio of two reactants was 1:1 and the temperature was maintained at 40 °C.

A series of sulfo-group-containing acrylate copolymers (PHEMA) were synthesized via free radical copolymerization of AMPS, HEMA, EHA and MMA. AIBN-initiated bulk copolymerizations of monomers were carried out at 90 °C. The concentration of AIBN was fixed equal to 2×10^{-3} mol per mol of all monomers. The prepared PHEMA then reacted with Hip to introduce urethane groups and cross-linkable double bonds into the side chain of polymer, which led to a UV-curable copolymer named as U-PHEMA. Finally, the IU-PHEMA, a prepolymer for anti-fog coating, was obtained by ionization of U-PHEMA with KOH–methanol solution. The whole synthetic route is shown in Scheme 1.

In the experiment, a series of IU-PHEMA prepolymers were prepared to investigate the influence of AMPS content on anti-fog properties. Table 1 shows the amount of each component used in the reaction.

Table 1
Composition of IU-PHEMA in copolymerization.

No.	HEMA	EHA	MMA	AMPS	IPDI	HEMA	AMPS%
IU-PHEMA01	21.95	24.72	11.24	1.00	25.00	16.01	1%
IU-PHEMA03	21.95	22.72	11.24	3.00	25.00	16.01	3%
IU-PHEMA05	21.95	20.72	11.24	5.00	25.00	16.01	5%
IU-PHEMA07	21.95	18.72	11.24	7.00	25.00	16.01	7%
IU-PHEMA08	21.95	17.72	11.24	8.00	25.00	16.01	8%
IU-PHEMA10	21.95	15.72	11.24	10.00	25.00	16.01	10%

2.3. Preparation of anti-fog coating

The IU-PHEMA was mixed with photoinitiator and reactive diluents to obtain formulas. HDDA and EOTMPTA were chosen as the reactive diluents to increase the double bond content, and CD9051 and w190 were used to improve the adhesion of formula on glass. Then the formula was coated on clean substrates to obtain a transparent film. The compositions of all formulas were shown in Table 2.

2.4. Measurements

The number-average molecular weight (M_n) and molecular weight distribution or polydispersity index PDI (M_w/M_n) of the polymers were determined at 25 °C with WATERS GPC-1515(GPC), using DMF as eluent at a flow rate of 1.0 mL min^{-1}. The molecular weight and polydispersity index data were compared against broad standards of PEG. FT-IR spectra were recorded with a Bomem FTLA 2000-104 using the potassium bromide (KBr) disk sampling