

UV curable coatings with mesogenic side groups

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Abstract

Copolymers having liquid crystalline (LC) side groups were prepared by ultraviolet (UV) photo-polymerization of acrylic monomers with mesogenic groups, acrylic monomers, and acrylic oligomers. These copolymers were evaluated as coatings on metal substrates in view of enhancement of film hardness and flexibility. A non-LC copolymer, i.e., a copolymer without mesogenic units, was used as control. Extraordinary balances of elongation and hardness have been obtained from the coatings consisting of copolymers with an LC side group. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction

Polymers having mesogenic units are called liquid crystalline (LC) polymers, which exhibit an intermediate state between an ordered crystalline state and an anisotropic liquid state. Mesogenic groups in these polymers show orientational orders under certain conditions [1]. Polymers with rigid chains have been developed since the 1970s, and they have been commercialized as fibers and plastics with high modulus, strength, and thermal stability [2].

Polymers with LC side groups, in which mesogenic groups are connected with the flexible backbones, are generally versatile to take the LC state by adjusting spacer sizes and the type of mesogens. Many research studies have been carried out in this area since the late 1970s [3,4]. These research studies included the synthesis and phase behavior of polymers with LC side groups [5,6], the rheological properties of polymers with LC side groups in nematic or smectic states [7], and the structure–property relation and structural models for cross-linked polymers with LC side groups [8,9]. In addition, polymers with LC side groups obtained by radiation-induced polymerization have been

investigated [10–15]. Shannon investigated the UV photo-polymerization of colesteric acrylates [10]. Shindo and Uryu studied the solid-state polymerization of LC acrylic monomers by a low-energy electron beam [11,12]. Broer et al. studied the UV photo-polymerization of oriented LC acrylates [13–15]. They also investigated network polymers obtained from diacrylate. However, the interest in these research studies was on functional polymers but not coatings on metals.

There have been several studies on the potential application of LC polymers for coatings [16–21]. The targets of these studies are to enhance the rheological properties, the curing rate, and the properties of cured coatings by incorporating LC moieties into coating binders. Jones et al. has reported an extraordinary combination of hardness and impact resistance for coatings of mesogenic diols cross-linked with hexakis (methoxymethyl) melamine (HMMM) [16]. In addition, exceptional hardness, toughness, and adhesion were obtained for the coatings of a linear oligoester diol, which was prepared from the reaction of amorphous oligomers and *p*-hydroxybenzoic acid (PHBA), cross-linked with HMMM [17]. For acrylic LC polymers prepared by grafting PHBA onto –COOH functional polymers, their uncross-linked coatings [18] and cross-linked coatings with HMMM [19] exhibited higher

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performance as coatings and films. Gähde et al. reported that LC polyurethane was used as a primer on steel substrates and evaluated the adhesion, i.e., the wet adhesion stability increased [21].

Application of prepainted systems, in which steel sheets are coated prior to the forming process, is increasing, because they are an environmental friendly process which eliminates painting after forming. On the contrary, requirements for prepainted steel sheets have accordingly become more severe. The most important technical challenge for prepainted steel sheets is to obtain paint films that are flexible and hard enough to provide the necessary scratch resistance, etc., to the finished products.

An objective of this study is to investigate the potential utility of LC polymers as coatings for prepainted steel sheets. UV photo-polymerization was used in the curing of coatings for the following reasons. (1) Polyacrylates with mesogenic side groups, which are the main body of the polymer with LC side groups, can be prepared by UV photo-polymerization. (2) UV curable coatings and their process are also environmental friendly, because they can reduce volatile solvents and decrease the energy required to cure coatings compared with conventional thermal curing [22,23]. UV-curable coatings, in general, provide hard, less flexible coating films due to the high cross-link density and the internal stress derived from the short curing period.

Based on the above background, the authors investigated the effect of LC side groups on coatings by preparing acrylic copolymers with different LC side groups, i.e., different spacer lengths and different kinds of mesogens (Fig. 1). The authors evaluated their potential utility for metal coatings. The LC groups mentioned above are expected to be bound into cross-linking structures and then to impart

improved toughness, hardness, and flexibility of the final film.

2. Experimental

2.1. Materials

As shown in Fig. 1, LC monomers consisting of an acryloyl group, a spacer, and a mesogen were synthesized according to the method described in Section 2.2.

Lauryl acrylate, trimethylol propane triacrylate, and butyl acrylate were obtained from Aldrich and were used as received. *N*-Vinyl-2-pyrrolidone, aliphatic urethane acrylate oligomer (GAFGARD 238) from GAF Corp., and epoxy acrylate oligomer (Ripoxy VR-60) from Showa Highpolymer Co. were used as received too. Solvents obtained from Aldrich were used after distillation. 2,2-Dimethoxy-2-phenyl acetophenone (Irgacure 651 from Ciba-Geigy Corp.) was used as received.

Cold-rolled steel sheets (0.5 mm thick) manufactured by NKK corp. were used as substrates. After a dry-in-plate chromate coating, an epoxy primer (WP-3 from NOF Corp.) was coated and cured (peak metal temperature 210 °C, dry film thickness 5 μm), then top-coated and cured by UV.

2.2. Preparation of LC monomers

Four types of monomers with different mesogens and/or spacer lengths were prepared. Synthesis was carried out according to the literature methods [6,24]. Reaction schemes are shown in Scheme 1. The chemical structure and elementary analysis data are shown in Fig. 2 and Table 1. Elementary analysis data matched the calculated data well.

2.3. Preparation of coatings and coated metals

The obtained monomers were blended with acrylic monomers, acrylic oligomers, solvents, and a photo-initiator, then coated on substrates by wire wound bars and cured by UV irradiation at 60 °C for 30 s. A TOSCURE 401 (Toshiba Lightning and Technology Corp.) equipped with a 400 W high pressure Hg lamp (intensity 26.8 mW/cm²) was used for the curing.

2.4. Measurements of thermal and mechanical properties

Infrared (IR) spectra were taken using a Cygnus 25 FTIR (Mattson International). Samples were cast on NaCl plates. Differential scanning calorimetry (DSC) measurements of the LC monomers and the LC coatings were carried out using a SSC-5000 thermal analysis system with a DSC-200 unit (Seiko Instruments). Measurements were carried out at a heating rate of 10 °C/min under a nitrogen purge. The tem-

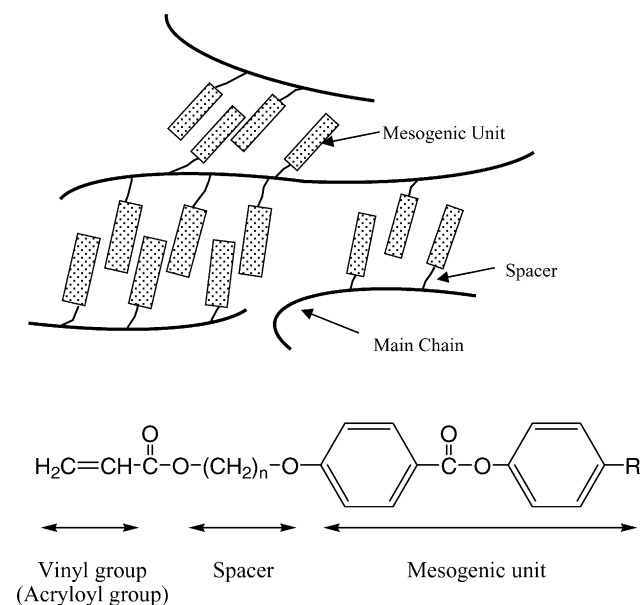


Fig. 1. Structure of the side chain liquid crystalline polymer and the monomer unit.

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