Green Chemistry of Polyurethanes

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Abstract—The current state and the main problems in a new field of macromolecular compounds—green chemistry of polyurethanes—based on cyclocarbonate reactions with amines, including those with cyclocarbonate-containing oligomers from renewable vegetable raw material, are briefly discussed.

Keywords: green chemistry, non-isocyanate polyurethanes, cyclocarbonates, renewable raw materials, oligomers from vegetable oils

INTRODUCTION

Polyurethane adhesives, coatings, and sealants occupy a very significant segment of the world market of polymer materials used for these purposes [1]. At present, polyurethanes and all the components necessary for their synthesis—aliphatic and aromatic isocyanates, polyisocyanates, and hydroxyl-containing polyethers and polyesters (both linear and branched)—are manufactured from petroleum feedstocks.

The classical method of synthesis of polyurethanes, which was developed 70 years ago and is based on the reaction of NCO groups of di- or polyisocyanates with OH groups of di- or polyols, is not environmentally ideal, primarily because of the high toxicity of isocyanates derived from primary amines via their phosgenation. In this context, producer countries in this field of polymer chemistry have been actively working to develop alternative ways to synthesize not only isocyanates, without the use of phosgene, but also polyurethanes themselves without the use of isocyanates and petroleum feedstock. Gradually, a new area in this field—green chemistry of polyurethanes—has emerged. A number of recent reviews [2–6] have shown the relevance of research in the field of non-isocyanate polyurethanes and prospects of development of this field of polymer chemistry.

In the present paper, some current problems of green chemistry of polyurethanes based on non-isocyanate preparation methods using renewable plant raw materials are briefly discussed.

RESULTS AND DISCUSSION

Reactions of Cyclocarbonates and Amines as a Route to Non-isocyanate Polyurethanes

Among the few reactions that may be a basis for the synthesis of non-isocyanate polyurethanes, the reaction of primary amines with cyclocarbonates can be considered to be very promising:

Polyurethanes formed by this reaction contain hydroxyl groups (secondary I or primary II), which contribute to their hydrolytic stability due to intramolecular hydrogen bonding and open the routes for modifications of these polymers [7]. Only in recent years has the potential of this reaction in polyurethane synthesis promoted intense study of the kinetics and mechanism of cyclocarbonates aminolysis [8–13]. There are two routes of cyclocarbonate aminolysis proceeding simultaneously. The first one involves one amine molecule, and the second involves two molecules, with the second amine molecule acting as a catalyst of a proton transfer stage. At this stage, a proton is added to the carbonyl group of cyclocarbonate. The rate of the reaction with two amine molecules participating is much higher, and the reaction activation energy is about half that of the reaction with one amine molecule involved. The addition of amine to cyclocarbonate is accelerated in the presence of...
hydroxyl- and carbonyl-containing compounds and carboxylic acids acting as bifunctional catalysts of proton transfer.

Oligomers with cyclocarbonate groups generally are derived from epoxy-containing synthons. At the same time, catalytic fixation of CO₂ with epoxides is considered to be quite promising:

This reaction can be also attributed to green chemistry and used for solving the problem of use of CO₂ that has been arising in the world in recent years due to global warming. The most cost-effective way to use CO₂ is as a source of carbon for a variety of organic compounds, monomers, solvents, fuels, etc. The main difficulty in use of CO₂ is its inertness in most of reactions, which requires the use of active reagents or high energy costs. Therefore, only few processes have been brought to industrial application. However, even these processes cannot be considered sufficiently effective. Searches for new reactions of carbon oxide fixation are always being carried out. One of these reactions is addition of CO₂ to epoxides to form cyclocarbonates. The advantage of this reaction is the absence of side products. Despite the seeming simplicity of the reaction, CO₂ fixation with epoxides is a complex process catalyzed by alkali metal salts, Lewis acids and bases, quaternary ammonium and phosphonium salts, transition metal complexes, ionic liquids, etc. [14, 15].

Along with the reaction of CO₂ with epoxides and the subsequent reaction of the formed cyclocarbonates with amines, the use of renewable natural materials—in particular, triglycerides of various unsaturated fatty acids, i.e., the components of plant oils—is involved in the green chemistry of polyurethane. These are easily converted via oxidation into epoxidized analogues and, subsequently, via the reaction with CO₂ into corresponding oligomers with cyclocarbonate functional groups in the chain. The method and conditions for the synthesis of these oligomers from plant raw materials are described in the literature [16–18]. In addition, the content of unsaturated and saturated acids in most plant oils (soybean, sunflower, palm, linseed, olive, rapeseed, etc.) is well known [19, 20]. However, for controlled synthesis of polyurethanes from plant oils, not only the numbers and contents of unsaturated bonds in the initial triglycerides, but also the compositions of triglycerides after oxidation and carbonation and their functionality at epoxy and cyclocarbonate groups, are crucial. The molecular structure and properties of the final product cross linked in the reaction with an amine directly depend on these parameters. Typically, there are no data on this question for specific triglyceride oils in the literature. For example, it has been suggested [5] that triglycerides of soybean oil and its epoxy derivatives formed via the oxidation of double bonds of the natural product have the following structure:

At the same time, it has been suggested that all the epoxy groups are converted into cyclocarbonate groups because of 100% carbonization under the action of CO₂: 

Cyclocarbonate-Containing Triglycerides of Plant Oils are Renewable Raw Materials for New Urethanes