Polymer 106 (2016) 128–139

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

From rigid and flexible foams to elastomers via Michael addition chemistry

Mark F. Sonnenschein [a, *], Jenny B. Werness [a, 1], Kshitish A. Patankar [a], Xin Jin [b], Matthew Z. Larive [a]

[a] The Dow Chemical Co., Corporate Research and Development, Midland, MI, 48674, USA
[b] The Dow Chemical Co., Corporate Research and Development, Freeport, TX, 77541, USA

ARTICLE INFO

Article history:
Received 29 August 2016
Received in revised form
24 October 2016
Accepted 27 October 2016
Available online 28 October 2016

Keywords:
Foams
Elastomers
Non-isocyanate
Michael-addition

ABSTRACT

Carbon-Michael chemistry can be used to produce rigid and viscoelastic foams, as well as flexible elastomers capable of effective function in traditional polyurethane applications. A simple synthetic procedure is provided for converting polyol oligomers and acetoacetate functionalized esters into useful building blocks. In this article detailed procedures for producing foams and elastomers by a carbon-Michael approach, the resulting mechanical properties of these polymeric materials, and structure property relationships for crosslink density are provided. These materials and techniques can potentially be substituted for isocyanate systems, especially in cases where isocyanates may not be advisable due to environmental, health, or safety concerns.

1. Introduction

Industrial consumers of isocyanates have adapted to challenges associated with handling hazards by protecting workers from inhalation and skin contact [1,2]. This is routinely achieved through commonsense safeguards for worker protection. However, the recent appearance of consumer products containing unreacted isocyanates means that consumers, unregulated contractors, and unknowing bystanders have the risk for unintended primary exposure or incidental secondary exposure to isocyanates. Occupational exposure has been documented to result in dermal and inhalation sensitization [3]. For this reason the United States Environmental Protection Agency [4], several U.S. state agencies [5], and The European Commission [6] have instituted or proposed limits to the use of isocyanates. Despite this scrutiny, there is little probability that urethane chemistry will be soon displaced due to its very high effectiveness, and its highly advantaged economies of scale. However, there may be instances when, due to specific requirements or circumstances, polyurethane chemistry is unworkable, and in those cases, it is very beneficial to have useful alternatives which may function in place of an isocyanate containing solution.

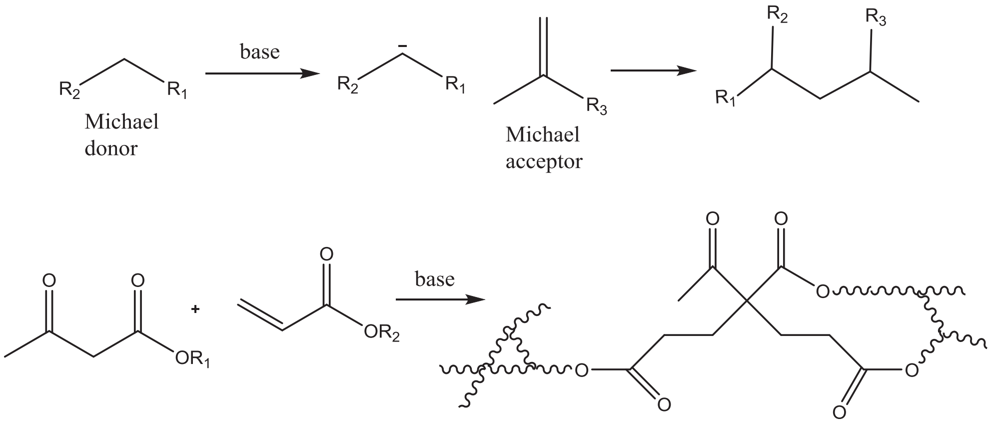
Carbon-Michael (CM) chemistry has received attention for its ability to produce polymers and macromolecular networks at room temperature with appropriate catalysis [7,8]. CM chemistry has been explored and optimized by us [9,10] and others [11,12] into prospective new polymer product families. Michael addition chemistry as envisioned here is a two-component addition involving mixing the two sides with a catalyst and any surfactants, blowing agents, or fillers as necessary. In bulk the reaction proceeds with increasing speed as the exothermic bond formation provides an adiabatic rate enhancement. The CM addition proceeds with no formation of condensation by-products, which is a simplifying aspect to achieving complete conversion. In this regard, carbon-Michael chemistry is similar to aspects of polyurethane chemistry. Unlike polyurethane chemistry, there is no block copolymer formation, and therefore no opportunity to take advantage of two-phase composite structural fortification [13,14]. The result is that structural integrity of materials made from CM chemistry will be provided via crosslinked network formation, or incorporation of fillers in a manner similar to silicone polymer products.

CM chemistry involves the addition of a nucleophile to an electrophilic carbon-carbon double bond. When the nucleophile is a carbanion it is conventional to use the term carbon-Michael, in contrast to the aza-Michael addition of an amine to an electrophilic

---

* Corresponding author.
E-mail address: mfsonnenschein@dow.com (M.F. Sonnenschein).
[1] Current address: 3M Research and Development, Maplewood, MN 55119.

http://dx.doi.org/10.1016/j.polymer.2016.10.054
0032-3861/© 2016 Elsevier Ltd. All rights reserved.



Scheme 1. The Carbon-Michael reaction and its extension to polymer network formation.

carbon double bond [15,16], or thiol-ene for the addition of a thiol to an alkene [17–20]. In a typical CM reaction, the nucleophile (known as the Michael donor) is added to the electron deficient carbon-carbon double bond (known as the Michael acceptor) to create a new carbon-carbon single bond (Scheme 1). The nucleophilic carbanion can be formed by deprotonation of a carbon adjacent to an electron withdrawing group (eg. R^1 and R^2 = carbonyl, nitrile etc.). This carbanion can then attack the electron-deficient carbon-carbon double bond (R^3 = carbonyl, etc) to result in polymer step growth.

Creation of the carbanion on the Michael donor requires a base strength commensurate with the acidity of the Michael donor. Esters (pKa ~24) and ketones (pKa ~19) require base strength incompatible with most reacting systems. However, the presence of an additional proximal electron withdrawing group lowers the pKa to an acceptable level such that weaker, more conventional bases can be employed. A variety of Michael donors can be envisioned using this structural requirement such as β-ketoesters (also called acetoacetates pKa ~11) and malonic esters (pKa ~13). Deprotonation of these Michael donors give carbanions, which are sufficiently nucleophilic to readily react with some Michael acceptors. Michael acceptors reactive with acetoacetates/malonic esters are generally constrained to activated alkenes with vicinal electron withdrawing groups such as acrylates. When polyacetoacetates and polyacrylates are used, highly crosslinked polymeric systems are formed [21].

Initial efforts to implement carbon-Michael chemistry were aimed at replacement of polyurethane coatings [22]. Strong bases such as metal hydroxides and alkoxides, or quarternary ammonium salts were used to initiate thermoset network formation. The resulting coatings were found to have hardness and print resistance comparable to polyurethane coatings. Systems formulated with weaker bases were subsequently developed [23].

This article provides explicit procedures for making multifunctional acetoacetates, which can be combined with the myriad of commercially available polyacrylates to result in rigid and flexible foams depending on the molecular weight between crosslinks. Foaming procedures, formulations, and resulting properties are also provided. Additionally, thermoset polyester elastomers can be produced with properties adjustable by choice of spacers between functional units.

2. Experimental

2.1. Materials

Glycerol, *tert*-butylacetoacetate (*t*-butyl AcAc), and hydroquinonethoxyether were purchased from Sigma-Aldrich. Di-trimethylolpropane tetraacrylate (SR355) and Bisphenol A epoxy diacrylate (CN104Z) were obtained from Sartomer. Trimethylolpropane triacetoacetate (TMP triACAC, Lonzaman™ AATMP) was obtained from Lonza Group Ltd. Blowing Agent HFC 245fa was obtained from Honeywell International. The surfactant Tegostab™ 8469 was obtained from Evonik Industries. Polyols IP625, IP 9001, IP 585, Voranol™ 360, Voranol™ RN482, UNOXOL™ diol, Voranol 270, Voranol 470X, Voranol 230-112, Voranol 3150, Voratec SD 301, Voranol 4735, and Voranol 3136 were obtained from Dow Chemical. Functionalized fillers were generously provided by Dow Corning (Midland, MI) and Evonik Industries (Parsippany, NJ). All other chemicals were obtained from Sigma-Aldrich and used as received.

Table 1

Starting polyol, used in this work for preparation of poly AcAc building blocks for carbon-Michael foam and elastomer preparation. Molecular weights are number average. Functionality is the number of OH groups per molecule or polymer chain.

Starting polyol	Functionality	Polyol MW (g/mol)	MW AcAc functionalized polyol (g/mol)
Glycerin	3	92.1	344.2
IP 625	3	637.5	889.6
HQEE	2	198.1	366.2
IP 9001	2	488	656.1
Voranol™ 360	4.5	701.2	1113.0
Voranol RN 482	6	702	1206.2
UNOXOL diol	2	144.1	312.2
Voranol 270	3	708.6	960.7
IP 585	3.3	973.8	1259.5
Voranol 470x	3.5	417.9	712.0
Voranol 230-112	3	1497	1749.1
Voranol 3150	3	1008	1260.1
Voratec™ SD 301	3	1080	1332.1