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The aza-Michael reaction as an alternative strategy to generate advanced silicon-based (macro)molecules and materials

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ABSTRACT

Aza-Michael reaction is a simple and accessible addition reaction performed at moderate temperature, possibly without a catalyst and without releasing by-products. Its versatility allows designing specific structures thanks to the availability of a multitude of Michael acceptors and Michael donors. The reaction rate of the aza-Michael reaction can be improved by adding different co-reactants (polar protic solvents, catalysts) and/or adjusting the external energy sources (e.g. moderate to high temperatures or high pressures). Here, we show that this addition reaction is efficient for modifying or curing silicon-containing molecules, oligomers and polymers. The pros and cons of applying the aza-Michael reaction to silicon-containing molecules (including alkoxysilanes and PDMS) are highlighted. A large variety of intermediates such as coupling agents, reactive diluents, and sol-gel precursors prepared by the aza-Michael reaction are presented. Finally, applications of these, including products ranging from functional silicone intermediates to soft (unfilled) elastomers, are reported.

Contents

Abbreviations: 1°amine, primary amine; 2°amine, secondary amine; 3°amine, tertiary amine; Ac, acetyl group; Alk, alkyl group; APTMS, aminopropyltrimethoxysilane; BF, base formulation; cP, centipoise; DABCO®, 1,4-diazobicyclo [2.2.2] octane; DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene; DMA, dimethylacetamide; DMF, dimethylformamide; DMPS, dodecamethylpentasiloxane; DP, degree of polymerization; DSC, differential scanning calorimetry; E, Young's modulus; EB, electron beam; ESO, epoxidized soybean oil; EWG, electron-withdrawing group; FTIR, Fourier transform infrared spectroscopy; GC, gas chromatography; GC–MS, gas chromatography coupled with mass spectrometry; HFIP, hexafluoropropan-2-ol; HY, compound having hydrogen-bond accepting and donating abilities (amines alcohols); IPA, isopropanol; IR, infrared; JIS, Japanese industrial standard; k, rate constant; K, equilibrium constant; M, concentration units (mol L^{-1}); MEK, methyletherketone; MPa, megapascal; M_w, molecular weight; NMR, nuclear magnetic resonance; Pa, Pascal; PAMAM, polyamidoamine; PDMS, polydimethylsiloxane; PDO, 1,2-propanediol; PEG, poly(ethyleneglycol); PET, polyethylene terephthalate; POSS, polyoctahedral silsesquioxanes; PR, Piers-Rubinsztajn; PUR, polyurethane; PVP, polyvinylpyrrolidone; *r*, molar ratio; REACh, Registration Evaluation Authorization and restriction of Chemicals; RIM, reaction injection molding; RT, room temperature; RTV, room-temperature vulcanization; SEC, size-exclusion chromatography; SM, surface modifier; TFE, 2,2,2-trifluoroethanol; THF, tetrahydrofuran; TMPTA, trimethylolpropane-triacrylate; UV, ultraviolet; v, kinetic rate; VS, versus; WCA, water contact angle; wt, weight.

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1. Introduction

The aza-Michael reaction is one of the most fundamental reactions in organic chemistry, widely employed for the synthesis of bioactive molecules or building blocks in total synthesis. This addition reaction, discovered in 1874 [1], involves a nucleophile, more specifically an amine (Michael donor), and an electron deficient alkene molecule (Michael acceptor) such as acrylates [2–4], acrylamides [5,6], vinyl ketones [7,8], vinyl sulfones [9,10], vinyl phosphonates [11–13], acrylonitrile [14,15], and so on. This conjugate addition reaction benefits from mild reaction conditions, various compatible reagents, high conversions, 100% atom efficiency and the absence of side-products or toxic metal catalysts [16]. Almost all the criteria of the green chemistry principle described by P. Anastas and J. Warner [17] in the 90's are met by such a reaction, opening the way to the synthesis or modification of polymers in environmentally friendly conditions. Moreover, the aza-Michael reaction likely fulfils many of the pre-requisites of 'click-chemistry', a concept introduced by K.B. Sharpless in 2001 [18]. Such 'click' reactions were developed to generate large libraries of compounds for screening in discovery research. The aza-Michael addition thus belongs to two main pillars of modern chemistry that renders it almost unavoidable.

Over the past few decades, several reviews have reported catalyzed aza-Michael reactions involving acidic, basic, organometallic, and enzymatic catalysts [1] or asymmetric versions of the reaction involving enantioselective catalysts for the preparation of complex organic molecules [19–22]. Still, most studies are reporting product-sensitive results, without showing clear trends for a large family of compounds. Besides, issues such as selectivity in the case of multi-functional amines or *retro*-aza-Michael side-reactions, were hardly approached. Thus there is definitively plenty of room to go on fundamentally studying the aza-Michael reaction in order to better control it. Moreover, so far only one review published in 2006 showed the potential of the aza-Michael reaction as applied to the polymer domain [16]. A wide range of topologies, from linear to dendritic or hyperbranched polymers, can be simply generated. Note that polymer networks are reachable either by direct aza-Michael addition with multi-functional reagents, or by a two-step synthesis, i.e. aza-Michael addition followed by sol-gel, or UV cross-linking.

PDMS can be modified or cured using several specific condensation and addition reactions (Scheme 1) [23]. Most of them are metal or metalloid-catalyzed reactions: hydrosilylation is catalyzed by Platinum or Ruthenium-based complexes, hydrolysis/condensation reactions use tin derivatives, and the most recent Piers-Rubinsztajn reaction (PR) [24] is promoted by heavily fluorinated boron molecules. In the former, the catalyst is rapidly poisoned by nitrogen- or sulfur-containing compounds [25]. Polycondensation reactions suffer from sensitivity to moisture and the generation of volatiles (typically ethanol), in addition to being regulated by the REACh for catalyst toxicity. The PR reaction is straightforward in the lab, but the high reactivity of the boron catalyst makes its use quite tricky on a larger scale. In addition, the