

# Synthesis of novel polymer brushes of poly(acrylonitrile-*g*-*N,N'*-dimethylaminoethyl methacrylate) by nitrile modification

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**Abstract** Functional polymer brushes of poly(acrylonitrile-*g*-*N,N'*-dimethylaminoethyl methacrylate) were efficiently synthesized by a novel approach of combining Cu(0)-mediated controlled/“living” radical polymerization and nitrile click chemistry. The poly(acrylonitrile-*g*-*N,N'*-dimethylaminoethyl methacrylate) as a promising material exhibited excellent hydrophile–lipophile balance in the process of self-assembly and could autonomously develop the orderly structure micelle in *N,N'*-dimethylformamide/water mixture solvent for the potential application of a new drug delivery carrier. In the process of self-assembly, polyacrylonitrile acted as a backbone of the functional polymer brushes due to its hydrophobic feature and poly(*N,N'*-dimethylaminoethyl methacrylate) as the branch of functional polymer brushes due to its hydrophilic characteristic, which both were prepared by Cu(0)-mediated controlled/“living” radical polymerization with ethyl-bromoisobutyrate as initiator. Poly(*N,N'*-dimethylaminoethyl methacrylate) containing azide end group was synthesized by substitution reaction of poly(*N,N'*-dimethylaminoethyl methacrylate) containing bromine end groups with sodium azide in *N,N'*-dimethylformamide. The click reaction between the nitrile of polyacrylonitrile and the azide group of poly(*N,N'*-dimethylaminoethyl methacrylate) was carried out under ammonium chloride as catalyst in *N,N'*-dimethylformamide. The polymer was further confirmed by GPC, FTIR, <sup>1</sup>H NMR and TGA. Meanwhile, the micelles

with different morphologies were observed by TEM, and the particle diameter distribution of self-assembled micelle from the PAN-*g*-PDMAEMA brushes was determined by DLS.

**Keywords** Controlled/“living” radical polymerization (CRP) · Polyacrylonitrile · Polymer brushes · Self-assembly

## Introduction

In recent years, click chemistry [1–3] has attracted more and more attention due to its potential as a novel method for modification of materials with high efficiency [4–6], high selectivity [7, 8], high tolerance of oxygen, and simple product isolation without subsequent purification processing and harsh reaction conditions. Click chemistry has an excellent application in surface functionalization and surface-responsive materials [9, 10]. The click chemistry reaction under mild conditions was noticed by Sharpless in 2001 due to its high selectivity, high efficiency and no by-product. Nowadays, the Sharpless-type click reaction based on the Huisgen 1,3-dipolar cycloaddition is well developed into different types (i.e., a series of the reactions between alkynyl bonds and alkyl-azides, aryl-azides, and sulfonyl-azides). Oxazoles, triazoles and tetrazoles can be easily obtained via the Sharpless-type click reaction. Furthermore, Diels–Alder-type reactions and cycloaddition reaction can extensively promote the functionalization of polymer materials (Scheme 1).

CuAAC reaction is a simple and moderate reaction, which is currently widely used in polymer synthesis [11]. Misaka and co-workers have successfully prepared poly( $\delta$ -valerolactone) by combining click chemistry and

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