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A brief review of 'schizophrenic' block copolymers

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Abstract

Recent progress in the synthesis of so-called 'schizophrenic' water-soluble block copolymers is reviewed. The original report in this new sub-field involved a tertiary amine methacrylate-based AB diblock copolymer synthesized by group transfer polymerization that was both pH- and salt-responsive, allowing the formation of either A-core or B-core micelles in aqueous solution. A second example involved a poly(propylene oxide)-tertiary amine methacrylate diblock copolymer synthesized via atom transfer radical polymerization (ATRP) that exhibited both pH- and thermo-responsive behavior. More recently, several examples of wholly pH-responsive zwitterionic diblock copolymers (prepared via ATRP, usually using protecting group chemistry) have been reported, with their aqueous solution behavior being characterized with varying degrees of precision. The synthesis and characterization of purely thermo-responsive diblock copolymers is also discussed, along with the first example of an ABC triblock copolymer that is capable of forming a 'trinity' of micelles in aqueous solution at 20 °C simply by adjusting the solution pH. In this remarkable final example, the cores of the three types of micelles are formed by hydrophobic forces, polyion complexation and hydrogen bonding, respectively.

Keywords: Block copolymer; Micelle; Water-soluble polymers; Schizophrenic; Self-assembly

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1. Introduction

Since 1998 numerous examples of novel water-soluble diblock copolymers that exhibit so-called 'schizophrenic' character have been reported. That is, the copolymer chains can self-assemble in dilute aqueous solution in the absence of any organic co-solvent to form *two* distinct micelle structures. In each case, the individual blocks can be independently tuned to become either hydrophilic or hydrophobic by subtle adjustment of the solution temperature, solution pH or ionic strength. The phrase 'schizophrenic block copolymers' was coined by our research group to describe this behavior, which is not exhibited by conventional small molecule surfactants.

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2. Experimental

Full experimental details of the synthesis and aqueous solution characterization of each of the various literature examples of 'schizophrenic' diblock copolymers (see below) have already been published elsewhere [1–14] and the reader is referred to the original literature for further details. The chemical structures and acronyms of the various 'schizophrenic' diblock copolymers described in this review article are shown in Fig. 1.

3. First example of a 'schizophrenic' diblock copolymer

In the first reported example [1], the diblock copolymer was based on two tertiary amine methacrylates, namely 2-(diethylamino)ethyl methacrylate [DEA] and 2-(*N*-morpholino)ethyl methacrylate [MEMA] (see Fig. 2). These two monomers contain no labile protons and thus can be directly polymerized using group transfer polymerization [GTP], which is particularly well suited for the synthesis of controlled-structure methacrylic copolymers [15]. At pH 6 this PMEMA–PDEA diblock dissolved molecularly in dilute aqueous solution at 20 °C (under these conditions the neutral PMEMA block is hydrophilic and non-ionic, whereas the PDEA block is protonated and hence soluble as a cationic polyelectrolyte). At pH 8.5, the PDEA block is deprotonated and becomes hydrophobic, leading to PDEA-core micelles, as judged by dynamic light scattering (DLS) studies. On the other hand, if sufficient electrolyte is added to the original solution at pH 6, the PMEMA block can be selectively salted out to produce PMEMA-core micelles. The micelle structures postulated on the basis of chemical intuition (and prior knowledge of the aqueous solution behavior of the PMEMA and PDEA homopolymers) were confirmed using ^{1}H NMR spectroscopy: no PDEA signals were detected for the PDEA-core micelles and the PMEMA signals were suppressed for the PMEMA-core mi-

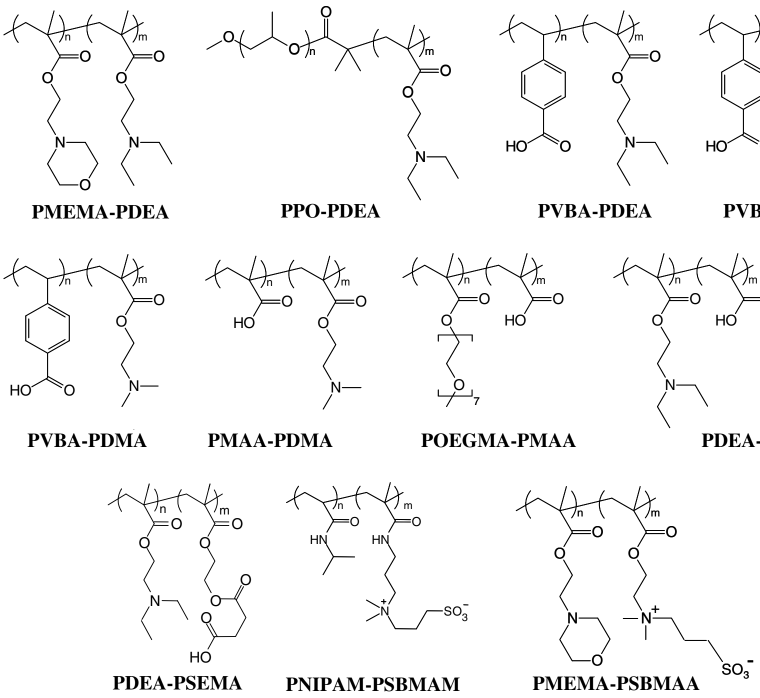

Fig. 1. Chemical structures and acronyms of the various 'schizophrenic' diblock copolymers discussed in this review article. In each case micellar self-assembly occurs in dilute solution on adjusting the pH, temperature or ionic strength.