NONLINEAR BLOCK COPOLYMERS SYNTHESIZED VIA CONTROLLED FREE RADICAL POLYMERIZATION

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The micellization behavior of amphiphilic block copolymers in aqueous media has received a great deal of attention in the past several decades. Double hydrophilic block copolymers (DHBCs) represent a new class of amphiphilic block copolymers, which can self-assemble into one or more types of micelles in aqueous solution if external conditions such as temperature, pH, and ionic strengths are finely tuned.

Recently Armes et al.[1] reported the preparation of the first examples of stimulus-responsive Y-shaped (AB_2) DHBCs, which can self-assemble into micelles with different dimensions to those formed by the linear diblock copolymers. Compared to Y-shaped block copolymers, H-shaped block copolymer of the A_2BA_2 type can be considered as the covalent linkage of the A block between two AB_2 block copolymers. Super-H-shaped block copolymer (A_3BA_3) can accordingly be considered as the linkage between two AB_3 block copolymers. A_nBA_n ($n > 3$) should be called star-*b*-linear-*b*-star block copolymers or pom-pom polymers.

The syntheses of nonlinear shaped (AB_n, A_nBA_n) block copolymers typically rely on anionic polymerization technique, which is always challenging due to the time-consuming purification of monomers, the unavoidable side reactions, and the necessity of quantitative addition of each reactant. Hadjichristidis et al.[2] and Knauss et al.[3] have done a lot of excellent work on this subject. With the advent of controlled free radical polymerizations, such as nitroxide-mediated polymerization (NMP), reversible addition-fragmentation chain transfer (RAFT), and atom transfer radical polymerization (ATRP), the syntheses of A_nBA_n ($n \geq 2$) block copolymers can be conducted in a much simpler manner through successive controlled free radical polymerizations or its combination with conventional living polymerization techniques such as cationic ring opening polymerization and anionic polymerization. Pan et al.[4] reported the synthesis of H-shaped $(PS)_2PEO(PS)_2$ via ATRP, they also reported the synthesis of $(PDOP)_2PS(PDOP)_2$ through a combination of RAFT and ring-opening polymerization (ROP), where PDOP is poly(1,3-dioxepane).[5] Just recently, An et al.[6] reported the preparation of asymmetric H-shaped [A_2BC_2, $(PS)_2PEO(PMMA)_2$] block copolymers via a combination of ATRP and living anionic polymerization, which represent a new development in the family of H-shaped block copolymers.

In this presentation, we report the syntheses and stimuli-responsive micellization behavior of a variety of nonlinear block copolymers (AB_2, A_2B, AB_4, A_2BA_2, A_4BA_4, AB, and ABA) with poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO), poly(*N*-isopropylacrylamide) (PNIPAM), poly(2-(diethylamino) ethyl methacrylate) (PDEA), poly(2-(dimethylamino)ethyl methacrylate) (PDMA), poly(ε-caprolactone) (CL), and poly(benzyl ether) dendrimers as the building units by employing ATRP, RAFT, ROP techniques or a combination of them. The synthesized nonlinear block copolymers include $PCL(PDMA)_2$, $(PCL)_2PDMA$, $PNIPAM(PDEA)_4$ $(PDEA)_2PPO(PDEA)_2$, $(PDEA)_4PPO(PDEA)_4$, $(PDEA)_4PEO$ $(PDEA)_4$, [G]-*b*-PNIPAM, and [G]-PNIPAM-[G], their chemical structures are shown in Figure 1.

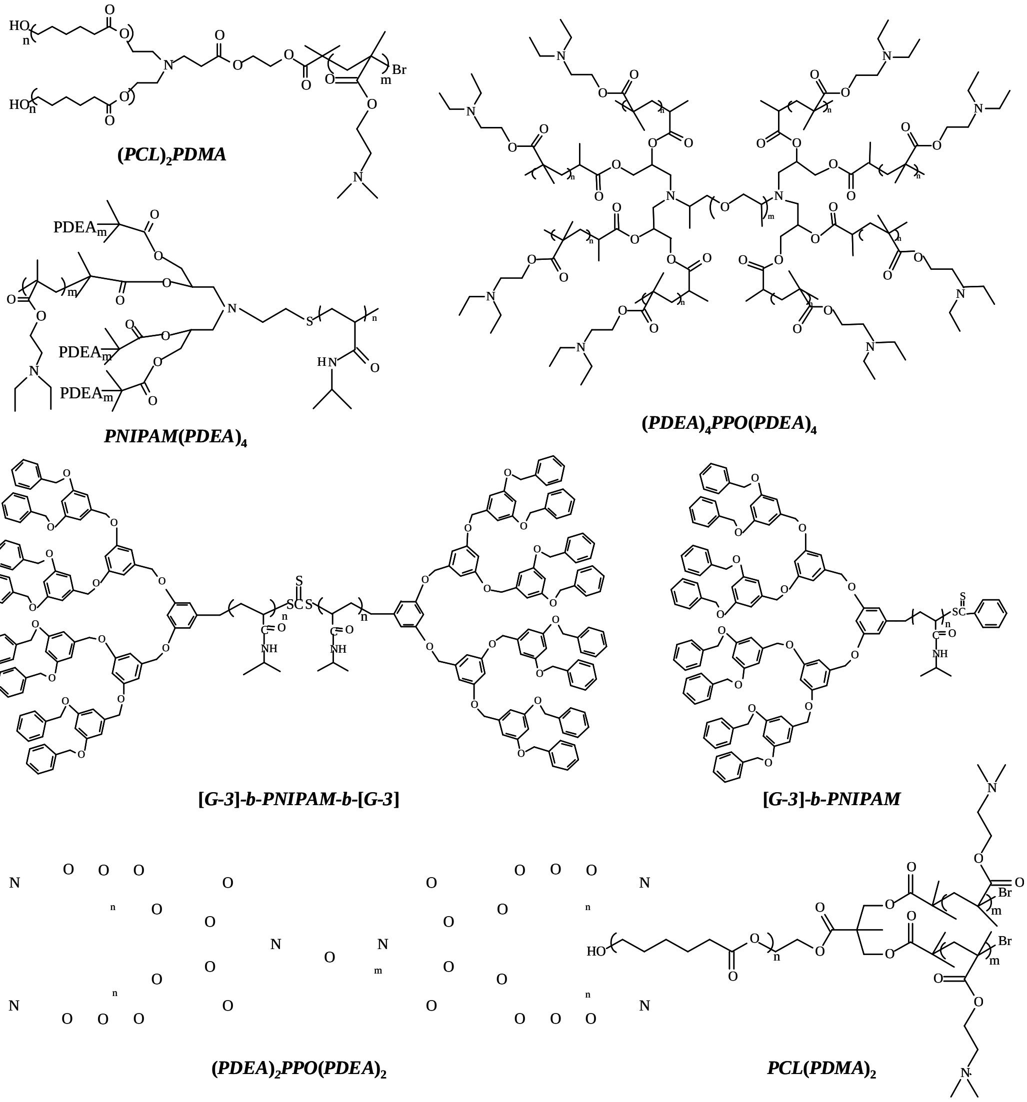

Figure 1. Chemical structures of nonlinear block copolymers synthesized in this study.

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