

Synthesis of well-defined amphiphilic poly(D,L-lactide)-*b*-poly(*N*-vinylpyrrolidone) block copolymers using ROP and xanthate-mediated RAFT polymerization

K. Ramesh^{a,b}, Avnish Kumar Mishra^a, Vijay Kumar Patel^a, Niraj Kumar Vishwakarma^a, Chandra Sekhar Biswas^a, Tapas Kumar Paira^c, Tarun Kumar Mandal^c, Pralay Maiti^d, Nira Misra^b, Biswajit Ray^{a,*}

^a Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi 221005, India

^b School of Biomedical Engineering, Institute of Technology, Banaras Hindu University, Varanasi 221005, India

^c Polymer Science Unit, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India

^d School of Material Science and Technology, Institute of Technology, Banaras Hindu University, Varanasi 221005, India

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ABSTRACT

Well-defined amphiphilic poly(D,L-lactide)-*b*-poly(*N*-vinylpyrrolidone) (PDLLA-*b*-PNVP) block copolymers were successfully prepared using ring-opening polymerization (ROP) and xanthate-mediated reversible addition-fragmentation chain transfer (RAFT) polymerization. Synthesized PDLLA-*b*-PNVP block copolymers were characterized by ¹H NMR spectroscopy and GPC. Spherical micelles of ~30.2 nm diameter were formed from the aqueous solution of amphiphilic diblock copolymer PDLLA₄₂-*b*-PNVP₆₃ as revealed by TEM and supported by ¹H NMR and light scattering. The critical micelle concentration value of the block copolymers, determined by fluorescence spectroscopy using pyrene as probe, increased with the increase in the chain length of PNVP block. The average hydrodynamic radius (*R*_h) of the micelles remained almost constant above the cmc value over the angles of scattering measurement. Thermal properties of these block copolymers were studied by TGA, DTA and DSC. Crystalline properties of these block copolymers were studied by WXR. D.

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1. Introduction

Synthesis of well-defined amphiphilic block copolymers using controlled radical polymerization (CRP) technique [1,2] has recently received considerable momentum owing to the potential application of these block copolymers in drug delivery [3], coatings [4–7], nanoparticle synthesis [8–13], colloidal stabilization [14–16], and as compatibiliser [17–19] for polymer blends. Synthesis of biocompatible and biodegradable amphiphilic block copolymer will be of immense interest in respect of its pharmaceutical and biomedical applications. Very recently, we have reported the controlled synthesis of well-defined amphiphilic diblock copolymers of ϵ -caprolactone (CL) and NVP by combining the controlled ROP of CL and the controlled xanthate-mediated RAFT polymerization of NVP [20]. In this respect, amphiphilic block copolymers containing a hydrophobic poly(D,L-lactide) (PDLLA) segment, which has biocompatibility and biodegradability [21–24], and

a hydrophilic poly(*N*-vinylpyrrolidone) (PNVP) segment, which has high water solubility, low toxicity, biocompatibility, complexation capability, cryo-protectivity, lyoprotectivity and antibiofouling properties, will be very interesting. D,L-lactide (DLA) is generally polymerized by ring-opening polymerization (ROP). On the other hand, *N*-Vinylpyrrolidone (NVP) can only be polymerized by radical polymerization due to the nonconjugation of its amide keto group with the vinyl group. Different controlled/living radical polymerization methods [25–37] have already been reported for the controlled synthesis of its homopolymer and block copolymers. Reports of the synthesis of such PNVP-*b*-PDLLA block copolymer are very few in the literature [38–40]. Leroux et al. [38] have reported first the synthesis and micellar characterization of PNVP-*b*-PDLLA block copolymers prepared by conventional radical polymerization of NVP using 2-isopropoxy ethanol initiator followed by conventional anionic ring-opening polymerization. Later, Luo et al. [39] have reported the synthesis and micellar characterization of PNVP-*b*-PDLLA block copolymer prepared through the combination of conventional radical polymerization of NVP in the presence of 2-mercaptoethanol chain transfer agent, and the ROP of DLA using anionic ring-opening polymerization. Recently, Xiong et al. [40]

* Corresponding author.

E-mail address: biswajitray2003@yahoo.co.in (B. Ray).

have reported the synthesis, characterization, and degradation of PDLLA-*b*-PNVP-*b*-PDLLA triblock copolymer prepared through the ROP of DLLA using dihydroxy PNVP as macro-initiator and dibutyl tin dilaurate (DBTDL) as catalyst. Here, we report the controlled synthesis of well-defined amphiphilic block copolymers of DLLA and NVP via the combination of the controlled ROP of DLLA and the controlled metal-free xanthate-mediated RAFT polymerization of NVP (Scheme 1). First, PDLLA with –OH end-group (PDLLA-OH) is synthesized using ROP. Then, the –OH end-group is converted to the corresponding –Br end group (PDLLA-Br) through a reaction with 2-bromopropionyl bromide. This –Br end-group is then converted to *O*-ethyl xanthate end group (PDLLA-X) through an ionic substitution reaction with potassium *O*-ethyl xanthate. Finally, the controlled RAFT polymerization of NVP is performed to synthesize well-defined amphiphilic PDLLA-*b*-PNVP block copolymers using a macro chain transfer agent PDLLA-X. Further, the self-assembly behavior of the resultant amphiphilic block copolymers is studied using ^1H NMR, fluorescence spectroscopy, transmission electron microscopy, and light scattering study. Thermal property of these block copolymers is also studied by thermo gravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimeter (DSC). Crystalline property of these block copolymers is also studied by the wide angle X-ray diffraction (WXRd) technique.

2. Experimental

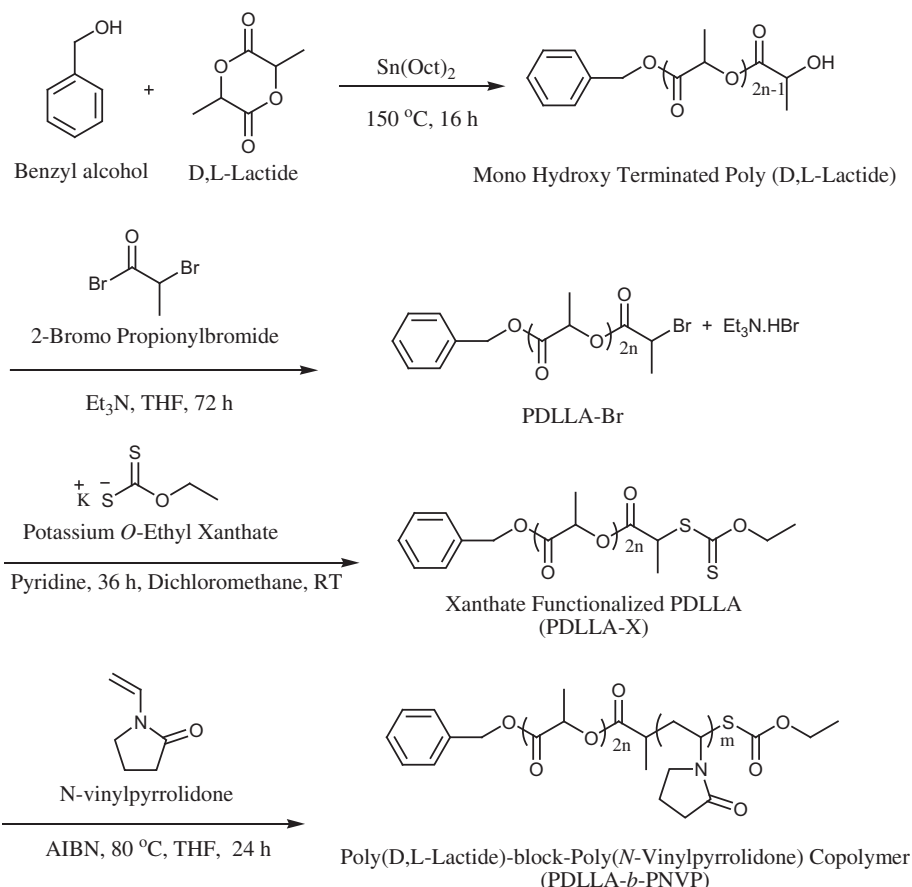
2.1. Materials

Triethylamine (Loba Chemie, Mumbai, India, 99%), 2-bromopropionyl bromide (Fluka, Israel, >97%), stannous 2-

ethylhexanoate [$\text{Sn}(\text{Oct})_2$] (Aldrich, St Louis, USA, 99%), diethyl ether (s.d.fine, Mumbai, India), hexane (CDH, Mumbai, India), methanol (Loba Chemie, Mumbai, India, 99%), sodium hydrogen carbonate (Loba Chemie, Mumbai, India), ammonium chloride (s.d.fine, Mumbai, India), anhydrous magnesium sulfate (Loba Chemie, Mumbai, India) were used as received. Benzyl alcohol (s.d.fine, Mumbai, India, 99%) was dried over CaO and then distilled under reduced pressure. (D,L-lactide) (DLLA) (Aldrich, St Louis, USA, 99%) was recrystallized from ethyl acetate. *N*-Vinylpyrrolidone (Aldrich, St Louis, USA, 99%) was dried over anhydrous magnesium sulfate and distilled under reduced pressure. 2, 2'-Azobis(isobutyronitrile) (AIBN) (Spectrochem, Mumbai, India, 98%) was recrystallized from methanol. Tetrahydrofuran (THF) (Loba Chemie, Mumbai, India) was dried and fractionally distilled from sodium and benzophenone. Ethanol (Saraya Distillery, India) was stirred over CaO overnight and distilled over fresh CaO. Potassium *O*-ethyl xanthate was prepared according to our previous work [37].

2.2. General methods

^1H NMR spectra were recorded on a JEOL AL300 FTNMR (300 MHz) at room temperature in CDCl_3 or D_2O as solvent, and were reported in parts per million (δ) from internal standard tetramethylsilane or residual solvent peak. NVP monomer conversion (%) was determined using ^1H NMR spectroscopy in CDCl_3 by comparing the integrated peak area of the residual vinylic signals at 4.3–4.4 ppm (2H) and 7.0–7.1 ppm (1H) of the monomer with the peak area of the methylene protons adjacent to 'N' of pyrrolidone ring at 3.0–3.4 ppm (2H) of the corresponding polymer. The number-average molecular weight (M_n) and polydispersity index



Scheme 1. Synthesis of PDLLA-*b*-PNVP block copolymer via ROP and xanthate mediated RAFT polymerization methods.

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