Synthesis of *N*-vinylcarbazole–*N*-vinylpyrrolidone amphiphilic block copolymers by xanthate-mediated controlled radical polymerization

Chih-Feng Huang, Jeong Ae Yoon, and Krzysztof Matyjaszewski

Abstract: Amphiphilic block copolymers poly(*N*-vinylcarbazole)-*b*-poly(*N*-vinylpyrrolidone) (PNVK-*b*-PNVP) were prepared by xanthate-mediated reversible addition-fragmentation chain transfer (RAFT) polymerization. Both the PNVK and PNVP macroinitiators and the resulting block copolymers had molecular weights close to theoretical values, predicted for efficient initiation, in the range of M_n = 30 000 to 90 000. The block copolymers dissolved in several organic solvents but, depending on their composition, in methanol formed either micelles or large aggregates, as confirmed by dynamic light scattering. The presence of globular aggregates was confirmed by tapping mode atomic force microscopy.

Key words: amphiphilic block copolymer, RAFT, living radical polymerization, micelle.

Résumé : On a préparé des copolymères à bloc amphiphiles poly(*N*-vinylcarbazole)-*b*-poly(*N*-vinylpyrrolidone) (PNVK-*b*-PNVP) par une réaction de polymérisation de transfert de chaîne avec addition-fragmentation réversible (TCAR) catalysée par le xanthate. Les valeurs des poids moléculaires des deux macroinitiateurs PNVK et PNVP ainsi que des copolymères à bloc qui en ont résulté étaient proches des valeurs théoriques prévues pour une initiation efficace, de l'ordre de M_n = 30,000 à 90,000. Les copolymères à bloc se dissolvent dans plusieurs solvants organiques; toutefois, dans le méthanol, suivant leur composition, il y a formation de micelles ou de gros agrégats décelés par la diffusion dynamique de la lumière. La présence d'agrégats globulaires a aussi été confirmée par la spectroscopie en mode de forces atomiques.

Mots-clés : copolymère à bloc amphiphile, transfert de chaîne avec addition-fragmentation réversible (TCAR), polymérisation radicalaire vivante, micelle.

[Traduit par la Rédaction]

Introduction

The preparation and properties of amphiphilic block copolymers, with hydrophilic and hydrophobic blocks, is currently an area of active study. Amphiphilic block copolymers form various supramolecular structures such as micelles, cylinders, or vesicles through self-organization and self-assembly and are being evaluated in numerous applications including emulsifiers, dispersants, and surfactants.[1] Potential uses also include microcontainers for delivery of hydrophobic materials or templates for syntheses of materials with nanosized features.

The aim of this study is to synthesize amphiphilic block copolymers using *N*-vinylcarbazole and *N*-vinylpyrrolidone (PNVK-*b*-PNVP). PNVK, a carbazole-containing polymer, is a photoconductive material with good charge-transport properties that has found applications as a photoreceptor, light-emitting diode, and photorefractive material.[2] On the other hand, PNVP, the water-soluble block, has been used in medical, pharmaceutical, and cosmetic applications, due to its low toxicity and good biocompatibility.[3] This indicates that PNVK-*b*-PNVP could be an interesting conductive polymer which could be processed in water. The nanophase separation of the amphiphilic block copolymer could result in a conductive PNVK segment embedded in an insulating PNVP matrix. There are only a few reports on water processable conductive block copolymers because of the difficulties with synthesis.[4] To prepare well-defined amphiphilic block copolymers, a controlled/living polymerization technique is required.[5] Although both NVK and NVP can be polymerized by radical mechanisms, the controlled radical polymerizations of NVK and NVP have not been yet thoroughly studied due to the low reactivity of non-conjugated vinyl monomers.

In general, block copolymers can be prepared by three routes: sequential monomer addition;[6] chain-end coupling of separately prepared blocks;[7] or transformation of chain ends of polymers prepared by one mechanism into initiating moi-

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Scheme 1. Synthesis of PNVK-*b*-PNVP amphiphilic block copolymers via xanthate-mediated RAFT polymerization.

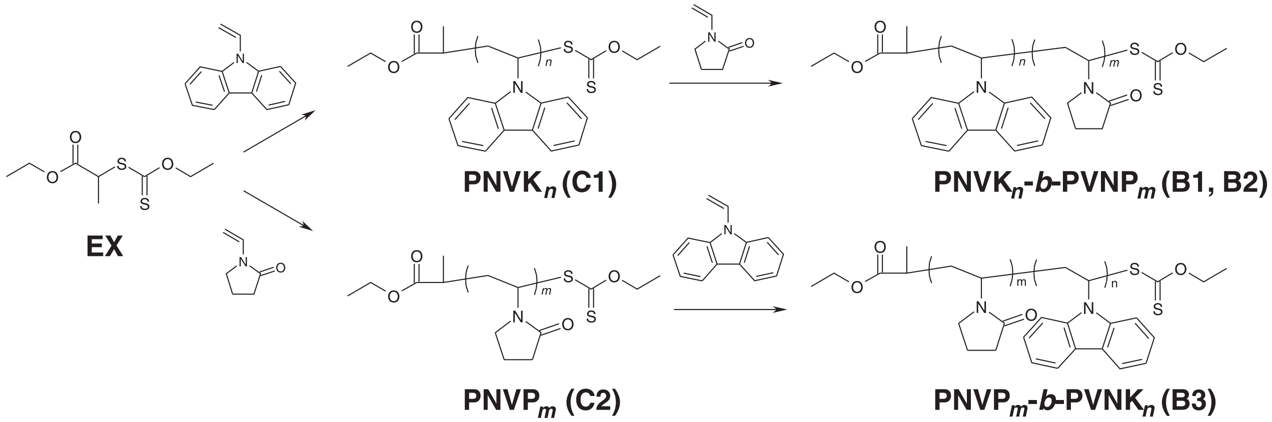


Table 1. Compositions and molecular weights of macroinitiators and block copolymers.

Entry	Composition[f]	$M_{\mathrm{n,\ theory}}$[g]	$M_{\mathrm{n,\ NMR}}$	$M_{\mathrm{n,\ GPC}}$	PDI
C1[a]	PNVK$_{31}$	6200	—	6300[h]	1.28
C2[b]	PNVP$_{46}$	5200	—	5300[i]	1.28
B1[c]	PNVK$_{31}$-*b*-PNVP$_{269}$	39 200	35 800	35 400[i]	1.35
B2[d]	PNVK$_{31}$-*b*-PNVP$_{573}$	70 900	69 200	88 000[i]	1.52
B3[e]	PNVP$_{46}$-*b*-PNVK$_{139}$	32 400	32 100	21 700[i]	1.35

[a] [NVK]/[EX]/[AIBN] = 43/1/0.5, 66 wt% of 1,4-dioxane to NVK, 60 °C, 4 h, conversion 71.0%.

[b] [NVP]/[EX]/[AIBN] = 150/1/0.35, 20 wt% of anisole to NVP, 60 °C, 4.5 h, conversion 30.1%.

[c] [NVP]/[C1]/[AIBN] = 600/1/0.5, 33 (*v*/*v*)% of anisole to NVP, 60 °C, 3.1 h, conversion 50.3%.

[d] [NVP]/[C1]/[AIBN] = 600/1/0.5, 33 (*v*/*v*)% of anisole to NVP, 60 °C, 20.9 h, conversion 98.1%.

[e] [NVK]/[C2]/[AIBN] = 150/1/0.5, 50 wt% of anisole to (NVK + C2), 60 °C, 26.2 h, conversion 93.9%.

[f] Homopolymer compositions were based on molecular weights measured by GPC. Block copolymer compositions were based on their macroinitiator composition and the NMR spectra of block copolymers.

[g] Molecular weights based on monomer conversion.

[h] GPC in THF, PS standards.

[i] GPC in DMF, PMMA standards.

eties for the chain propagation of the second monomer.[8] Previous attempts to prepare well-defined PNVK or PNVP homopolymers using one of the CRP methods has involved a degenerative transfer radical mechanism,[9] ATRP,[10] or Co-mediated polymerization.[11] Only a few studies describe chain extension from either PNVK or PNVP homopolymers to prepare block copolymers.[12] Regardless of the potentially interesting properties, block copolymers of PNVK and PNVP (PNVK-*b*-PNVP) have not been yet prepared, since the synthesis of well defined PNVK-*b*-PNVP block copolymers is challenging, owing to the low reactivity of both NVK and NVP. The low reactivity of NVK and NVP and the low stability of the propagating radicals indicate that a degenerative transfer process, such as reversible addition-fragmentation chain transfer (RAFT) polymerization, could be best suited for conducting a controlled polymerization. For this study, we selected a xanthate-type mediating agent, since it was successfully employed for RAFT polymerization of less active monomers in previous studies.[12d]

Experimental

Materials

N-Vinylpyrrolidone (NVP, 99%, Sigma-Aldrich) was dried over anhydrous magnesium sulfate and purified by distillation under reduced pressure. *N*-vinylcarbazole (NVK, 97%, Sigma-Aldrich) and 2,2′-azobis(isobutyronitrile) (AIBN, 99%, Sigma-Aldrich) were recrystallized twice from methanol. All solvents were purified by distillation prior to use. *S*-(2-Ethyl propionate)-*O*-ethyl xanthate (EX)[13] was synthesized according to the literature procedure. Briefly, potassium *O*-ethyl xanthate (4.75 g, 2.9×10^{-2} mol) was dissolved in 25 mL of ethanol with ethyl 2-bromopropionate (4.74 g, 5.3×10^{-2} mol) for 20 h at room temperature. The crude product was purified by extraction with diethyl ether – water followed by column chromatography using hexane – ethyl acetate 95:5 (*v*/*v*) as eluent to give a yellow oil. Yield: 3.0 g (51%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 4.63 (q, 2H), 4.37 (q, 1H), 4.20 (q, 2H), 1.56 (d, 3H), 1.41 (t, 3H), 1.28 (t, 3H).

RAFT polymerization of NVK (C1)

3.41 g of NVK (17.6 mmol), 91.0 mg of EX (0.410 mmol), 34.0 mg of AIBN (0.207×10^{-3} mmol), and 8 mL of anisole were charged to a Schlenk flask. The molar ratio of NVK–EX–AIBN was 43:1:0.5. The mixture was deoxygenated by three freeze–pump–thaw cycles. The flask was placed in an oil bath thermostated at 60 °C for a required time period. Samples were withdrawn via a syringe for the measurement of monomer conversion and molecular

Fig. 1. Kinetic plots, evolution of molecular weights and polydispersities with conversion, and GPC traces for the synthesis of B1 and B2 (a, b, and c) and B3 (d, e, and f). Dashed lines (- - -) in (a) and (d) are least square linear fits. Solid lines (—) in (b) and (e) represent theoretical molecular weights vs. monomer conversion. Red triangles in (b) and (e) represent M_n values calculated based on block copolymer using ^{1}H NMR.

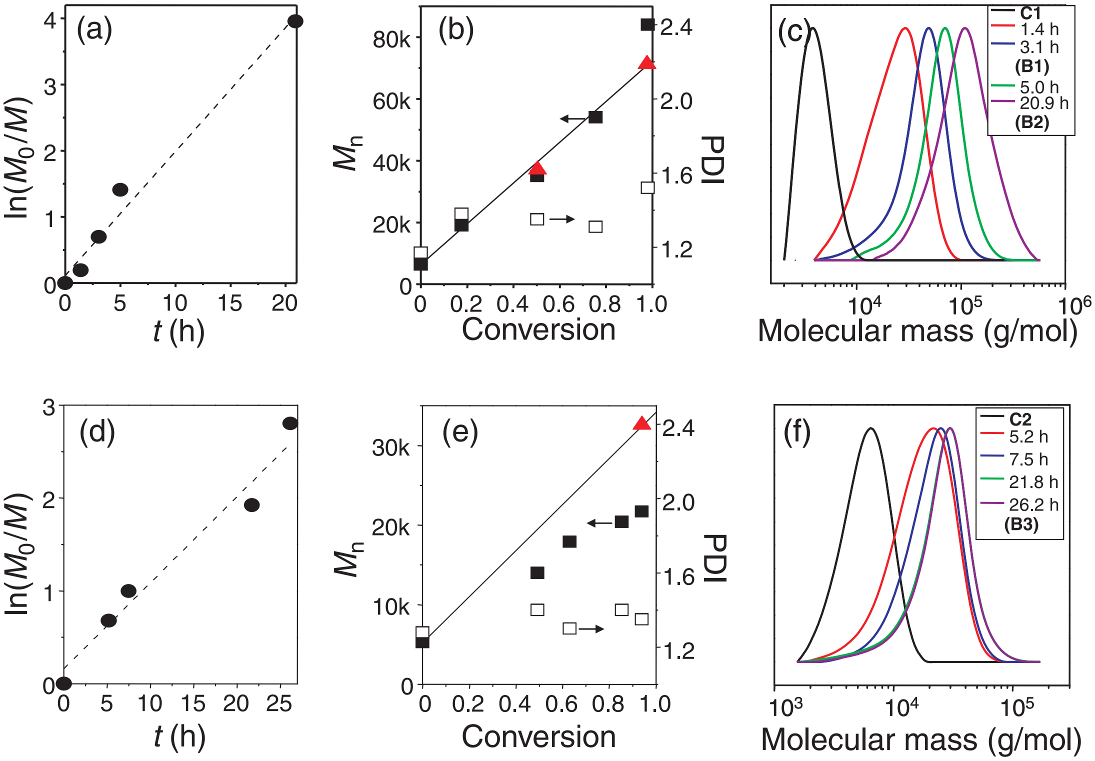


Table 2. Hydrodynamic diameters (nm) measured in various solvents at room temperature.

Solvent	DC[a]	B1 (PNVK$_{31}$-*b*-PNVP$_{269}$)	B2 (PNVK$_{31}$-*b*-PNVP$_{573}$)	B3 (PNVP$_{46}$-*b*-PNVK$_{139}$)
Anisole	4.3	315 (1.751)	2377 (0.540)	10.3 (0.425)
CHCl$_3$	4.8	7.86 (0.417)	12.9 (0.441)	9.34 (0.140)
THF	7.5	9.21 (0.390)	14.4 (0.304)	9.67 (0.170)
MeOH	33.0	44.0 (0.129)	64.0 (0.334)	774 + precipitation

Note: Average volume distribution. Numbers in parentheses are coefficients of variation.

[a] Dielectric constant.

weight of polymer by GPC with DMF or THF as eluent. The reaction was quenched by placing the flask in an ice bath, exposing to air, and diluting with THF to provide the PNVK–EX macromolecular chain transfer agent (C1). The crude polymer was purified by filtering through an alumina column followed by precipitation in hexane. Conversion = 71% (by NMR); $M_{\text{n, theor}}$ = 6200 g/mol, $M_{\text{n, TFH GPC}}$ = 6300 g/mol (PDI = 1.28).

RAFT polymerization of NVP (C2)

10.0 mL of NVP (10.4 g, 93.7 mmol), 139 mg of EX (0.626 mmol), 4.1 mg of AIBN (0.220 mmol), 2.5 mL of anisole were charged to a Schlenk flask. The mole ratio of NVP–EX–AIBN was 150:1:0.35. The mixture was deoxygenated by three freeze–pump–thaw cycles. The flask was placed in an oil bath thermostated at 60 °C for the desired time period. The rest of the procedure was the same as that for the preparation of C1. Conversion = 30% (by NMR); $M_{\text{n, theor}}$ = 5200 g/mol, $M_{\text{n, DMF GPC}}$ = 5300 g/mol (PDI = 1.28).

Chain extension of PNVK (C1) by RAFT polymerization of NVP forming a block copolymer

3.04 mL of NVP (3.18 g, 28.6 mmol), 0.300 g of C1 ($M_{\text{n, THF GPC}}$ = 6300 g/mol, PDI = 1.28, 47.6 × 10^{-3} mmol), 3.90 mg of AIBN (23.7 × 10^{-3} mmol), and 1.56 mL of anisole were charged to a Schlenk flask. The mole ratio of NVP–C1–AIBN was 600:1:0.5. The mixture was deoxygenated by three freeze–pump–thaw cycles and then was placed in an oil bath thermostated at 60 °C for the required time period. Monomer conversion and molecular weight were tracked by GPC with DMF as eluent. At the desired conversion, the reaction was quenched and the polymer was purified by filtering through an alumina column followed by precipitation in hexane. B1 conversion = 50% (by GPC); $M_{\text{n, theor}}$ = 39 200 g/mol, $M_{\text{n, DMF GPC}}$ = 35 400 g/mol

Fig. 2. DLS profile for PNVK-*b*-PNVP block copolymer (**B1**, **B2**, and **B3**) in chloroform and methanol. Blue line: PNVP block, Red line: PNVK block.

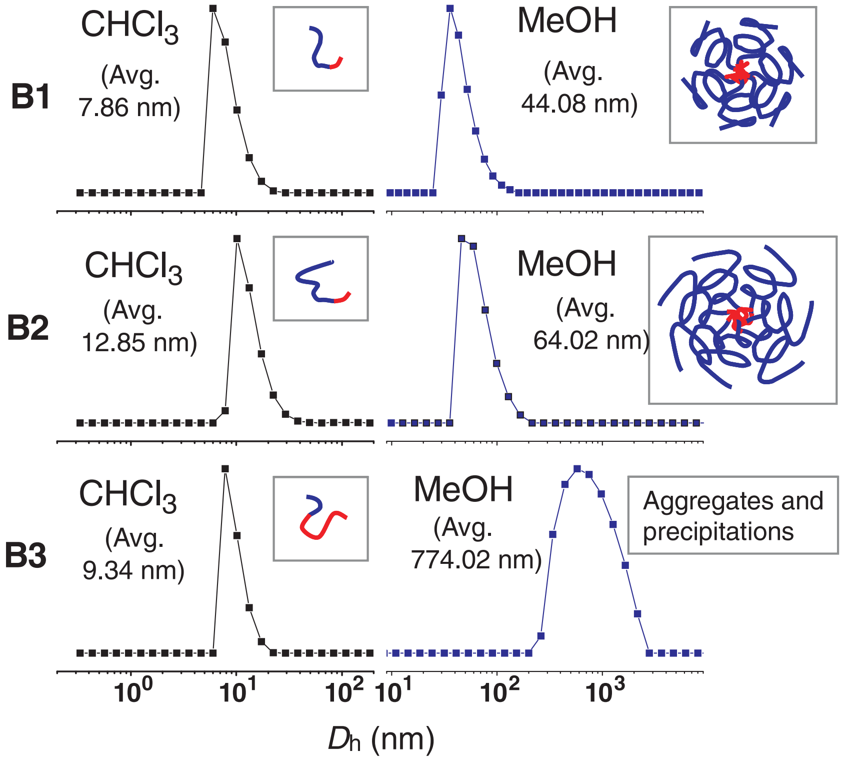
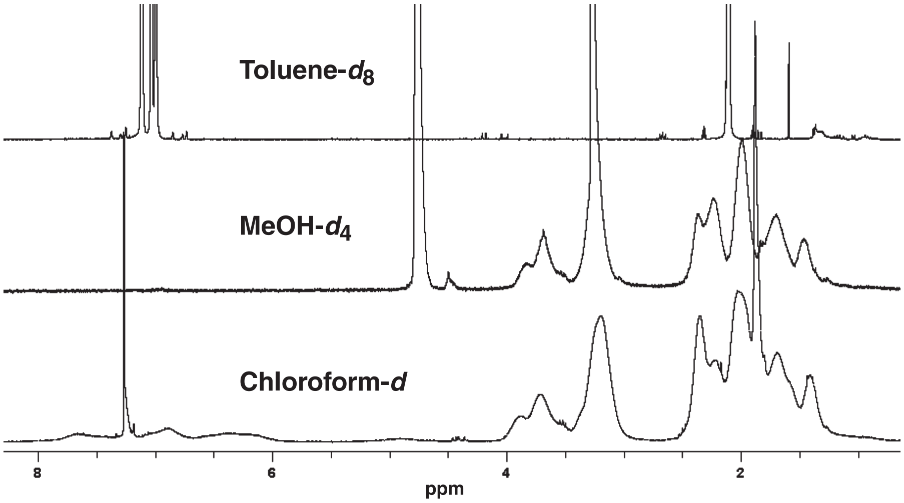


Fig. 3. ^{1}H NMR spectra of B1 in different solvents, toluene-d_8, MeOH-d_4, and chloroform-*d*.



(PDI = 1.35). B2 conversion = 98% (by GPC); $M_{\mathrm{n,\ theor}}$ = 70 900 g/mol, $M_{\mathrm{n,\ DMF\ GPC}}$ = 88 000 g/mol (PDI = 1.52).

Chain extension of PNVP (C2) by RAFT polymerization of NVK

1.09 g of NVK (5.65 mmol), 0.200 of C2 ($M_{\mathrm{n,\ DMF}}$ = 5300 g/mol, PDI = 1.28, 37.7 × 10^{-3} mmol), 3.10 mg of AIBN (18.9 × 10^{-3} mmol), and 2.60 mL of anisole were charged to a Schlenk flask. The mole ratio of NVK–C2–AIBN was 150:1:0.5. The mixture was deoxygenated by three freeze–pump–thaw cycles. The flask was placed in an oil bath thermostated at 60 °C for the required time. The rest of the procedure was the same as that for the block copolymerization of NVP from PNVK described above. B3 conversion = 94% (by GPC); $M_{\mathrm{n,\ theor}}$ = 32 400 g/mol, $M_{\mathrm{n,\ DMF\ GPC}}$ = 21 700 g/mol (PDI = 1.35).

Analyses

The molecular weights and molecular-weight distributions were measured using GPC (Polymer Standards Services, columns (guard, 10^5, 10^3, and 10^2 Å)) with DMF (containing 5 mmol/L LiBr) as eluent at 50 °C or with THF as eluent at 35 °C. The flow rate was kept at 1.00 mL/min and a differential refractive index (RI) detector (Waters, 2410) was used. Toluene was used as the internal standard to correct for any fluctuation in eluent flow rate. The molecular weight

Fig. 4. 3D images of height mode AFM at different conditions. B1: (a), (b), and (c), B3: (d), (e), and (f).

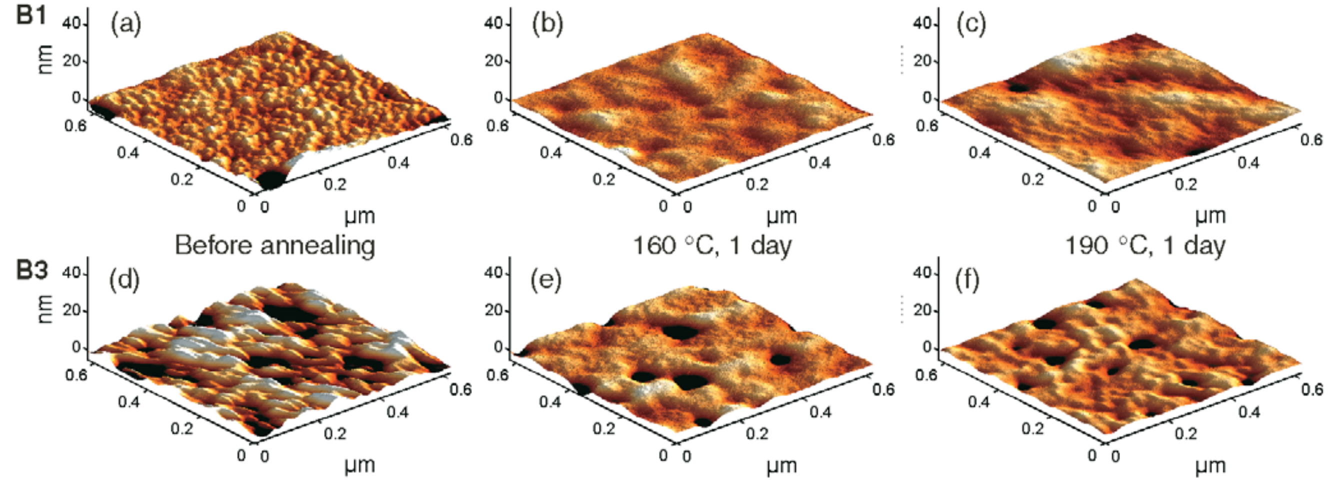
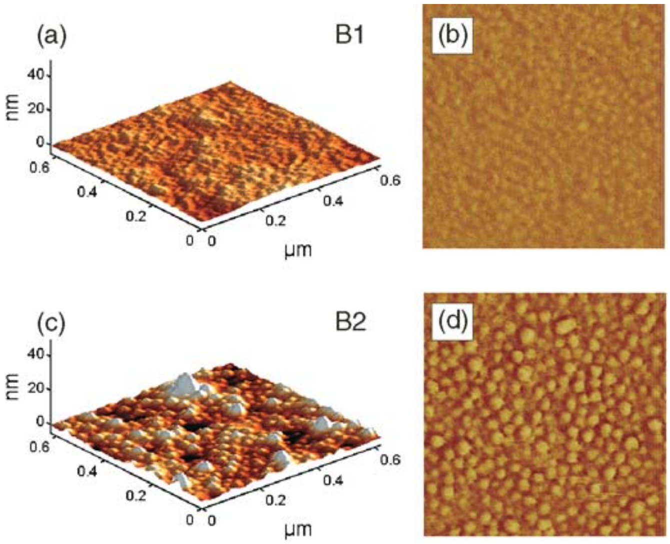


Fig. 5. 3D height mode AFM images (left column) and phase mode AFM images (right column) of B1 (a, b) and B2 (c, d) after drop casting of DMF solution and drying. Phase image size: 0.6 µm × 0.6 µm.



and the molecular-weight distribution were determined with a calibration curve based on linear PMMA (for DMF GPC line) or PS (for THF GPC line) standards using GPCWin software. Conversions were determined by NMR on a Bruker Avance^{TM} 300 MHz instrument or by an internal standard addition, injecting a known amount of monomer into reaction mixtures and following the peak area changes in GPC traces. Particle size and size distribution were measured by dynamic light scattering (DLS) on High Performance Particle Sizer, Model HP5001 from Malvern Instruments, Ltd. DLS measurements provide average diameter, D_{av}, and size distribution index, CV (coefficient of variation), which is defined as CV = $(S \times 100)/D_{av}$, where D_{av} is the mean diameter and S is the size standard deviation. Tapping mode AFM experiments were carried out using a Multimode Nanoscope V system (Veeco instruments). The measurements were performed in air using commercial Si cantilevers with a nominal spring constant and resonance frequency of 40 N/m and 330 kHz, respectively. The height and phase images were acquired simultaneously at a set-point ratio (A/A_0), in the range of 0.7–0.9, where A and A_0 refer, respectively, to the "tapping" and "free" cantilever amplitude.

Results and discussions

Synthesis

The synthesis of PNVK-*b*-PNVP block copolymers was conducted sequentially via the two alternative pathways shown in Scheme 1.

First, macromolecular chain transfer agents (CTAs), i.e., macroinitiators, were prepared by RAFT polymerizations using EX as a CTA. The molecular weights of the macroinitiators were measured by GPC and summarized in Table 1. The molecular weight of C1 measured by GPC (in THF using PS standards) (M_n = 6300, DP = 31) agreed well with the value estimated from monomer conversion ($\Delta[M]/[EX]_0$ = 43, DP = 31 at 71% conversion), assuming quantitative initiation. However, when the molecular weight was measured by GPC in DMF, a much smaller value (M_n = 3800, DP = 19) was obtained, presumably due to the formation of more compact polymer coils in DMF. A similar observation concerning a much smaller molecular weight of PS measured in DMF GPC, was reported previously.[14] The molecular weight of C2, determined by GPC (in DMF, PMMA standards), corresponded well to the theoretical molecular weight estimated from monomer conversion (DP = $\Delta[M]/[EX]_0$) with the assumption of the quantitative initiation efficiency. The molecular weight of the macroinitiators measured by GPC (in DMF) compared well with the molecular weight calculated by end group analysis of ^{1}H NMR spectra. For example, for another PNVP macroinitiator prepared under the same conditions as C2, M_n was calculated by end group analysis to be 4400 g/mol, and was measured by GPC to be 4500 g/mol (in DMF, PMMA standards). Furthermore, good agreement of experimental and theoretical molecular weights indicated that the number of new chains generated by decomposition of AIBN, coupling with CTA, and transfer process was small.

Chain extensions from the prepared macroinitiators were performed by RAFT polymerization of the second monomer. The molecular weight and polydispersity of each block copolymer and the block copolymer composition determined by NMR are summarized in Table 1. Figure 1 displays the kinetic plots, the linear change of molecular weight with conversion, and the evolution of GPC traces over time for each block copolymer. The chain extension reactions were carried out to over 90% monomer conversion for both pathways. The molecular weights of B1 and B2 measured by GPC (in DMF, PMMA standards) were very similar to the calculated molecular weights based on monomer conversion and ^{1}H NMR analyses. THF could not be used as GPC eluent for PNVP because it is isorefractive with PNVP. The molecular weight of B3, calculated from the ^{1}H NMR spectrum, was very close to that based on monomer conversion, assuming quantitative initiation. The values differed from the M_n by GPC (in DMF, PMMA standard) which can be attributed to the compact structure of the PNVK block (83 wt% in B3) in DMF, as was the case with the PNVK macroinitiator. The observed first-order kinetic plots and the very high efficiency of the chain extensions suggested the negligible contribution of possible side reactions such as formation of NVP dimers or elimination of xanthate end groups.[12e,15] This could be attributed to the simple structure of xanthate (EX), use of purified reagents, and the mild polymerization temperature (60 °C).

DLS and NMR studies

Particle-size distribution (volume vs. hydrodynamic diameter (D_h)) of each prepared block copolymer was studied by dynamic light scattering (DLS). Table 2 summarizes particle size distributions in various solvents having different polarities (represented in Table 2 by dielectric constant). The DLS profiles in two representative solvents, chloroform and methanol, are presented in Fig. 2.

All block copolymers displayed D_h values smaller than 15 nm in medium polarity solvents (chloroform and THF), implying dissolution of the block copolymers without formation of aggregates. However, when methanol was used as the solvent, the average particle size was much larger, ranging from 44 to 64 nm for B1 and B2, and resulted in larger aggregates (D_h > 700 nm) for B3 (some precipitation was visually observed). Methanol, a non-solvent for PNVK and a good solvent for PNVP, resulted in formation of micelles with PNVP as the major block in the outer shell (B1 and B2). With PNVK as the major block (B3), larger aggregates were formed, accompanied by precipitation. Assuming full stretching of PNVP chains, the calculated size of micelles for B1 and B2 should range from 150 nm to 390 nm (DP × (0.25 nm) × 2), respectively. Observed smaller diameters suggest coiled chains of PNVP, due to a less dense micelle structures (Fig. 2, insets). In contrast to methanol, anisole is a good solvent for PNVK because of aromatic interactions and a poor solvent for PNVP because of its weak hydrogen-bonding ability. As a result, while B3 dissolved as individual chains (D_h = 10.3 nm), B1 and B2, with PNVP as the major block, formed very large aggregates sized over 300 nm (cf. Table 2).

The change of solubility of the block copolymer in selective solvents was further confirmed by ^{1}H NMR measurements. The ^{1}H NMR spectra of B1 are shown in Fig. 3. In the spectrum measured in chloroform-*d*, a good solvent for both blocks, peaks from both PNVK block (4.5–8 ppm) and PNVP block (0.5–4.5 ppm) are well resolved. However, the peaks of PNVK block disappear when measured in MeOH-d_4, because of the insolubility of the PNVK block. Toluene-d_8 was selected as a nonpolar solvent instead of anisole. No appreciable peak was observed, proving the insolubility of the B1 to toluene owing to the large portion of polar PNVP block.

AFM studies

The phase separation in block copolymers was also observed by tapping mode AFM (Fig. 4). The block copolymers B1 and B3 were dissolved in chloroform (1 mg/mL) and solutions were drop-cast onto silicon wafers (1 cm × 1 cm), followed by drying under vacuum at room temperature overnight. The films of block copolymers were studied by AFM. Globular morphologies with dimensions of 37 nm and 49 nm were observed for B1 and B3. Although the dilute chloroform solutions of B1 and B3 did not contain aggregates (cf. DLS studies), they formed aggregates as concentration increased during the solvent evaporation. The polymer films were then annealed at 160 °C (Figs. 4b and 4e) and 190 °C (Figs. 4c and 4f), i.e., above the T_g of PNVP block (~120 °C) under vacuum. Because the annealing was conducted below the T_g of the PNVK block (~210 °C), phase separation could not be enhanced by thermal annealing. The aggregates, formed during the film formation, relaxed, as seen from smoothed surfaces after annealing.

The hypothesis that the globular morphology was generated by aggregation of polymers during the drying process was supported by another experiment. This time, block copolymers B1 and B2, with the same PNVK block but different chain length of PNVP, were dissolved in DMF, a good solvent for both blocks. Since DMF evaporates at a slower rate than chloroform, it should provide sufficient time for the copolymers to attain lower-energy morphologies. The height and phase mode AFM images of B1 and B2 in Fig. 5 were measured after drop casting and drying of DMF in a vacuum oven at room temperature. The average domain sizes of B1 and B2, obtained by 2D isotropic power spectral density analysis of height images, were 28 and 33 nm, respectively, indicating that the increase in the size of the domains is correlated with the dimensions of the PNVP blocks (DP = 269 vs. DP = 573).

Conclusion

Amphiphilic block copolymers with a hydrophobic PNVK block and a hydrophilic PNVP block were synthesized by xanthate-mediated RAFT polymerization by preparation of PNVK or PNVP macroinitiators and sequential chain extensions with the second monomer, i.e., NVP or NVK. The resulting block copolymers had low polydispersity and the molecular weight, measured by GPC and ^{1}H NMR, agreed well with the theoretical values. The particle-size distributions of the prepared block copolymers were measured in various solvents with different polarities. Block copolymers B1 and B2, with longer PNVP blocks, formed micelles in methanol whereas B3, with PNVK as the major block, formed larger aggregates and precipitates. AFM measurements of film samples revealed the block copolymers aggregated during the drying of films, even though the initial solution did not contain aggregates. Annealing the film samples at a temperature between the T_g of PNVK (210 °C) and PNVP (120 °C) yielded a smoother surface than before annealing but did not enhance the phase separation.

Acknowledgements

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References

(1) (a) Discher, B. M.; Won, Y. Y.; Ege, D. S.; Lee, J. C. M.; Bates, F. S.; Discher, D. E.; Hammer, D. A. *Science* **1999**, *284* (5417), 1143. doi:10.1126/science.284.5417.1143. PMID:10325219.; (b) Discher, D. E.; Eisenberg, A. *Science* **2002**, *297* (5583), 967. doi:10.1126/science.1074972. PMID:12169723.; (c) Jain, S.; Bates, F. S. *Science* **2003**, *300* (5618), 460. doi:10.1126/science.1082193. PMID:12702869.; (d) Zhang, Q.; Remsen, E. E.; Wooley, K. L. *J. Am. Chem. Soc.* **2000**, *122* (15), 3642. doi:10.1021/ja993941o.; (e) Alexandridis, P.; Olsson, U.; Lindman, B. *Langmuir* **1998**, *14* (10), 2627. doi:10.1021/la971117c.

(2) (a) Kido, J.; Hongawa, K.; Okuyama, K.; Nagai, K. *Appl. Phys. Lett.* **1993**, *63* (19), 2627. doi:10.1063/1.110402.; (b) Grazulevicius, J. V.; Strohriegl, P.; Pielichowski, J.; Pielichowski, K. *Prog. Polym. Sci.* **2003**, *28* (9), 1297. doi:10.1016/S0079-6700(03)00036-4.; (c) Wu, W.; Zhang, S.; Li, Y.; Li, J. X.; Liu, L. Q.; Qin, Y. J.; Guo, Z. X.; Dai, L. M.; Ye, C.; Zhu, D. B. *Macromolecules* **2003**, *36* (17), 6286. doi:10.1021/ma034513c.

(3) (a) Haaf, F.; Sanner, A.; Straub, F. *Polym. J.* **1985**, *17* (1), 143. doi:10.1295/polymj.17.143.; (b) Benahmed, A.; Ranger, M.; Leroux, J. C. *Pharm. Res.* **2001**, *18* (3), 323. doi:10.1023/A:1011054930439. PMID:11442272.; (c) D'Souza, A. J. M.; Schowen, R. L.; Topp, E. M. *J. Control. Release* **2004**, *94* (1), 91. doi:10.1016/j.jconrel.2003.09.014. PMID:14684274.

(4) (a) Kilbinger, A. F. M.; Feast, W. J. *J. Mater. Chem.* **2000**, *10* (8), 1777. doi:10.1039/b002899l.; (b) Henze, O.; Feast, W. J. *J. Mater. Chem.* **2003**, *13* (6), 1274. doi:10.1039/b212382g.; (c) Yan, L.; Tao, W. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *46* (1), 12. doi:10.1002/pola.22342.; (d) Hua, F.; Ruckenstein, E. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42* (9), 2179. doi:10.1002/pola.20042.; (e) Bhadra, S.; Khastgir, D.; Singha, N. K.; Lee, J. H. *Prog. Polym. Sci.* **2009**, *34*, 783.

(5) (a) Various living polymerizations and their application to the synthesis of block copolymers are covered in the following review articles: Matyjaszewski, K.; Müller, A. H. E. *Prog. Polym. Sci.* **2006**, *31* (12), 1039. doi:10.1016/j.progpolymsci.2006.09.002.; (b) Smid, J.; Van Beylen, M.; Hogen-Esch, T. E. *Prog. Polym. Sci.* **2006**, *31* (12), 1041. doi:10.1016/j.progpolymsci.2006.09.001.; (c) Hadjichristidis, N.; Iatrou, H.; Pitsikalis, M.; Mays, J. *Prog. Polym. Sci.* **2006**, *31* (12), 1068. doi:10.1016/j.progpolymsci.2006.07.002.; (d) Yagci, Y.; Tasdelen, M. A. *Prog. Polym. Sci.* **2006**, *31* (12), 1133. doi:10.1016/j.progpolymsci.2006.07.003.; (e) Bielawski, C. W.; Grubbs, R. H. *Prog. Polym. Sci.* **2007**, *32* (1), 1. doi:10.1016/j.progpolymsci.2006.08.006.; (f) Domski, G. J.; Rose, J. M.; Coates, G. W.; Bolig, A. D.; Brookhart, M. *Prog. Polym. Sci.* **2007**, *32* (1), 30. doi:10.1016/j.progpolymsci.2006.11.001.; (g) Braunecker, W. A.; Matyjaszewski, K. *Prog. Polym. Sci.* **2007**, *32* (1), 93. doi:10.1016/j.progpolymsci.2006.11.002.; (h) Yokozawa, T.; Yokoyama, A. *Prog. Polym. Sci.* **2007**, *32* (1), 147. doi:10.1016/j.progpolymsci.2006.08.001.; (i) Baskaran, D.; Mueller, A. H. E. *Prog. Polym. Sci.* **2007**, *32* (2), 173. doi:10.1016/j.progpolymsci.2007.01.003.; (j) Goethals, E. J.; Du Prez, F. *Prog. Polym. Sci.* **2007**, *32* (2), 220. doi:10.1016/j.progpolymsci.2007.01.001.; (k) Penczek, S.; Cypryk, M.; Duda, A.; Kubisa, P.; Slomkowski, S. *Prog. Polym. Sci.* **2007**, *32* (2), 247. doi:10.1016/j.progpolymsci.2007.01.002.; (l) *Controlled and Living Polymerizations: From Mechanisms to Materials*; Mueller, A. H. E., Matyjaszewski, K., Eds; Wiley-VCH: Weinheim, 2009.

(6) (a) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117* (20), 5614. doi:10.1021/ja00125a035.; (b) Davis, K. A.; Matyjaszewski, K. *Adv. Polym. Sci.* **2002**, *159*, 1. doi:10.1007/3-540-45806-9_1.; (c) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101* (9), 2921. doi:10.1021/cr940534g. PMID:11749397.; (d) Tsarevsky, N. V.; Matyjaszewski, K. *Chem. Rev.* **2007**, *107* (6), 2270. doi:10.1021/cr050947p. PMID:17530906.; (e) Matyjaszewski, K.; Tsarevsky, N. V. *Nature Chem.* **2009**, *1* (4), 276. doi:10.1038/nchem.257.

(7) (a) Hawker, C. J.; Wooley, K. L. *Science* **2005**, *309* (5738), 1200. doi:10.1126/science.1109778. PMID:16109874.; (b) Golas, P. L.; Matyjaszewski, K. *Qsar & Combin. Sci.* **2007**, *26* (11-12), 1116. doi:10.1002/qsar.200740059.

(8) (a) Yagci, Y.; Tasdelen, M. A. *Prog. Polym. Sci.* **2006**, *31* (12), 1133. doi:10.1016/j.progpolymsci.2006.07.003.; (b) Coca, S.; Paik, H.-.; Matyjaszewski, K. *Macromolecules* **1997**, *30* (21), 6513. doi:10.1021/ma970637b.; (c) Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* **1997**, *30* (14), 4241. doi:10.1021/ma970358o.; (d) Coca, S.; Matyjaszewski, K. *Macromolecules* **1997**, *30* (9), 2808. doi:10.1021/ma970073b.; (e) Matyjaszewski, K.; Beers, K. L.; Kern, A.; Gaynor, S. G. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36* (5), 823. doi:10.1002/(SICI)1099-0518(19980415)36:5<823::AID-POLA15>3.0.CO;2-I.; (f) Shinoda, H.; Matyjaszewski, K. *Macromolecules* **2001**, *34* (18), 6243. doi:10.1021/ma0105791.; (g) Davis, K. A.; Charleux, B.; Matyjaszewski, K. J. Polym. Sci., Part A: Polym. Chem. **2000**, *38*, 2274; (h) Pintauer, T.; Matyjaszewski, K. Coord. Chem. Rev. **2005**, *249*, 1155; (i) Shinoda, H.; Miller, P. J.; Matyjaszewski, K. Macromolecules **2001**, *34*, 3186; (j) Kowalewski, T.; Tsarevsky, N. V.; Matyjaszewski, K. J. Am. Chem. Soc. **2002**, *124*, 10632; (k) Oh, J. K.; Drumright, R.; Siegwart, D. J.; Matyjaszewski, K. Prog. Polym. Sci. **2008**, *33*, 448.

(9) (a) Ray, B.; Kotani, M.; Yamago, S. *Macromolecules* **2006**, *39* (16), 5259. doi:10.1021/ma060248u.; (b) Bilalis, P.; Pitsikalis, M.; Hadjichristidis, N. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44* (1), 659. doi:10.1002/pola.21198.; (c) Devasia, R.; Bindu, R. L.; Borsali, R.; Mougin, N.; Gnanou, Y. *Macromol. Symp.* **2005**, *229* (1), 8. doi:10.1002/masy.200551102.; (d) Mori, H.; Ookuma, H.; Nakano, S.; Endo, T. *Macromol. Chem. Phys.* **2006**, *207* (12), 1005. doi:10.1002/macp.200600070.; (e) Iovu, M. C.; Matyjaszewski, K. Macromolecules **2003**, *36*, 9346; (f) Sheiko, S. S.; Sumerlin, B. S.; Matyjaszewski, K. Prog. Polym. Sci. **2008**, *33*, 759; (g) Debuigne, A.; Poli, R.; Jerome, C.; Jerome, R.; Detrembleur, C. Prog. Polym. Sci. **2009**, *34*, 211; (h) Lutz, J.-F.; Boerner, H. G. Prog. Polym. Sci. **2008**, *33*, 1.

(10) (a) Lu, X. J.; Gong, S. L.; Meng, L. Z.; Li, C.; Yang, S.;

Zhang, L. F. *Polymer (Guildf.)* **2007**, *48* (10), 2835. doi:10.1016/j.polymer.2007.03.048.; (b) Hua, J.; Chen, D. B.; Yu, Y. L.; Xu, L.; Zhang, Y. F.; Jing, X. K.; Wu, A. Q.; Shi, L. *Polym. Bull.* **2002**, *48* (2), 135. doi:10.1007/s00289-002-0023-1.; (c) Brar, A. S.; Kaur, S. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44* (5), 1745. doi:10.1002/pola.21296.

(11) Kaneyoshi, H.; Matyjaszewski, K. *Macromolecules* **2006**, *39* (8), 2757. doi:10.1021/ma052746t.

(12) (a) Nguyen, T. L. U.; Eagles, K.; Davis, T. P.; Barner-Kowollik, C.; Stenzel, M. H. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44* (15), 4372. doi:10.1002/pola.21518.; (b) Hussain, H.; Tan, B. H.; Gudipati, C. S.; Liu, Y.; He, C. B.; Davis, T. P. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46* (16), 5604. doi:10.1002/pola.22882.; (c) Debuigne, A.; Willet, N.; Jerome, R.; Detrembleur, C. *Macromolecules* **2007**, *40* (20), 7111. doi:10.1021/ma0712908.; (d) Pound, G.; Aguesse, F.; McLeary, J. B.; Lange, R. F. M.; Klumperman, B. *Macromolecules* **2007**, *40* (25), 8861. doi:10.1021/ma0710075.; (e) Pound, G.; Eksteen, Z.; Pfukwa, R.; McKenzie, J. M.; Lange, R. F. M.; Klumperman, B. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46* (19), 6575. doi:10.1002/pola.22968.; (f) Mori, H.; Ookuma, H.; Endo, T. *Macromolecules* **2008**, *41* (19), 6925. doi:10.1021/ma801266h.; (g) Morton, K.; Graffe, A.; Maric, M. *Macromol. Chem. Phys.* **2007**, *208* (5), 496. doi:10.1002/macp.200600560.

(13) Kwak, Y.; Nicolay, R.; Matyjaszewski, K. *Macromolecules* **2009**, *42* (11), 3738. doi:10.1021/ma9005389.

(14) (a) Dong, H.; Tang, W.; Matyjaszewski, K. *Macromolecules* **2007**, *40* (9), 2974. doi:10.1021/ma070424e.; (b) Guillaneuf, Y.; Castignolles, P. J. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46* (3), 897. doi:10.1002/pola.22433.

(15) Huang, C. F.; Nicolay, Y.; Kwak, Y.; Chang, F. C.; Matyjaszewski, K. *Macromolecules* **2009**, *42* (21), 8198. doi:10.1021/ma901578z.