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Miktoarm Star Copolymers from the Chemical Stitching of Associating Block Copolymers

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ABSTRACT: A new method for the synthesis of miktoarm star copolymers is proposed. To demonstrate its viability, diblock copolymers, PA-*b*-PSCOOH, with a carboxyl-bearing short PSCOOH block, and triblock copolymers, PB-*b*-PNH_2-*b*-PB, with an amino-bearing short PNH_2 block, were synthesized and characterized. Here PA and PB denote poly(*tert*-butyl acrylate) and poly(methyl methacrylate), respectively. The carboxyl- and amino-bearing blocks of the copolymers associated with one another due to carboxylate and ammonium ion pairing in dichloromethane. The addition of a coupling agent caused the amino and carboxyl groups to amidize and resulted in the fusion of the associating chains, thus producing miktoarm copolymers μ-$(PA)_1(PB)_2$ and μ-$(PA)_2(PB)_2$. Factors affecting the relative and total yields of μ-$(PA)_1(PB)_2$ and μ-$(PA)_2(PB)_2$ formation were investigated.

I. Introduction

Miktoarm star copolymers, e.g. μ-(PA)(PB)(PC), exhibit interesting bulk block segregation patterns[1−5] and form compartmentalized micelles in block-selective solvents.[6−10] Various applications can be envisioned for the self-assembled, or block-segregated, structures of miktoarm star copolymers. Despite this, miktoarm star copolymers have not been studied extensively, except by Lodge, Hillmyer, and co-workers[8−11] as well as by Hadjichristidis and collaborators.[1,7] This is likely due to the difficulty associated with the synthesis of miktoarm star copolymers. In this paper, we report a new method for preparing miktoarm star copolymers.

In this method, we start with two block copolymers that bear short complementary blocks, which can associate with each other. The different block copolymers are therefore brought together due to the association of these short blocks. Reaction is then done to these associating blocks in order to stitch the different polymer chains together. If one of these block copolymers used is a triblock copolymer with the associating short block located in the middle, the stitched product should be a miktoarm star copolymer.

In order to demonstrate the viability of this strategy, we prepared carboxyl-bearing diblock copolymers of PA-*b*-PSCOOH as well as amino-bearing triblock copolymers of PB-*b*-$PGNH_2$-*b*-PB and PB-*b*-$PHNH_2$-*b*-PB. Here PA denotes poly(*tert*-butyl acrylate) (PtBA), PB denotes poly(methyl methacrylate) (PMMA), $PGNH_2$ denotes poly[(2-cinnamoyloxyethyl methacrylate)-*ran*-(2-glycinoyloxyethyl methacrylate)], $PHNH_2$ is poly[[(2-cinnamoyloxyethyl methacrylate)-*ran*-[2-(4′-(6″-aminohexylamino)-4′-oxo)butanoyloxyethyl methacrylate]], and PSCOOH denotes poly[(2-cinnamoyloxyethyl methacrylate)-*ran*-(2-(3′-carboxypropanoyloxy)ethyl methacrylate)].

In dichloromethane, PtBA-*b*-PSCOOH and PMMA-*b*-PNH_2-*b*-PMMA, where PNH_2 can be either $PGNH_2$ or $PHNH_2$, were associated with each other due to ion pairing between the carboxylate and ammonium ions.[12] The ions were formed as a result of proton transfer from the carboxyl to the amino groups. If one PA-*b*-PSCOOH chain was associated with one PMMA-*b*-PNH_2-*b*-PMMA chain, a three-armed cluster was formed (A → B, Scheme 2). The association of two PtBA-*b*-PSCOOH chains with one PMMA-*b*-PNH_2-*b*-PMMA chain resulted in a four-armed cluster (D → E). Amidization of the carboxyl and amino groups covalently stitched together the three-armed and four-armed clusters, B → C and E → F, to yield μ-$(PA)_1(PB)_2$ and μ-$(PA)_2(PB)_2$.

Cinnamoyl groups were introduced into the amino- and carboxyl-bearing blocks of the copolymers because we initially intended to take advantage of the photodimerization reaction of the cinnamoyl units[13−15] and thus stitch together the associated polymer chains. However, the amidization reaction was later found to be more efficient than the cinnamoyl dimerization reaction. Therefore, the cinnamoyl units performed no apparent function in this study.

While the preparation of miktoarm star copolymers from block copolymer precursors is new, the general concept of the preparation of architectural polymers from the assembly and reaction of block copolymer precursors is not. For example, we have reported on the controlled assembly of diblock copolymers in block-selective solvents into predominantly unimolecular or single-chain micelles. This was followed by the intrablock cross-linking of the collapsed block of these single-chain micelles to yield tadpole molecules. These tadpole-shaped molecules are diblock copolymers with a cross-linked spherical head block and a random-coil tail block.[16−18] We have also used this controlled block copolymer assembly and reaction methodology to prepare macrocycles in high purity and at high concentrations.[19]

Traditionally, miktoarm copolymers have been prepared from three general strategies. These include the "arms-first" approach, the "growing-from" approach, and the "hybrid" approach.[20,21] In the "arms-first" approach, the different arms are prepared from living or controlled polymerizations first and then linked together to yield the star polymers. If three arms, such as PA-Li, PB-Li, and PC-Li, are prepared by living anionic polymerization, the living chains bearing terminal anions can, for example,

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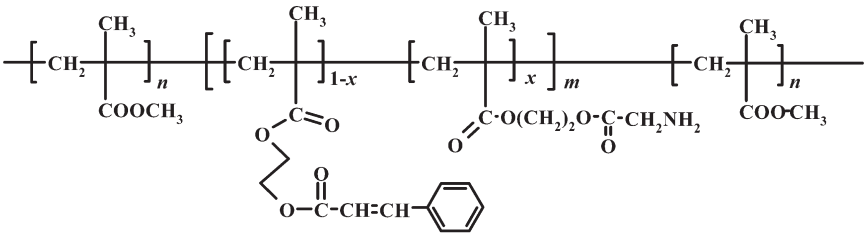
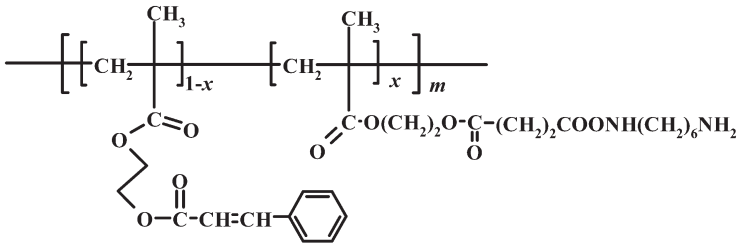
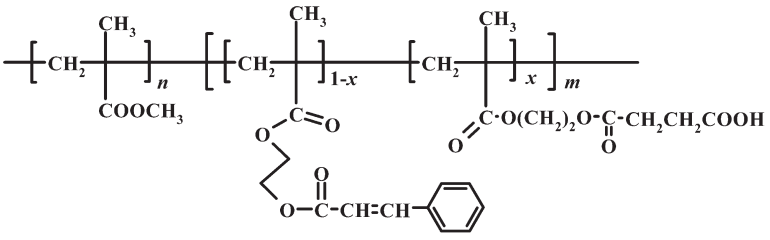
Scheme 1. Structures of Polymers and Polymer Blocks



PMMA-*b*-PGNH$_2$-*b*-PMMA

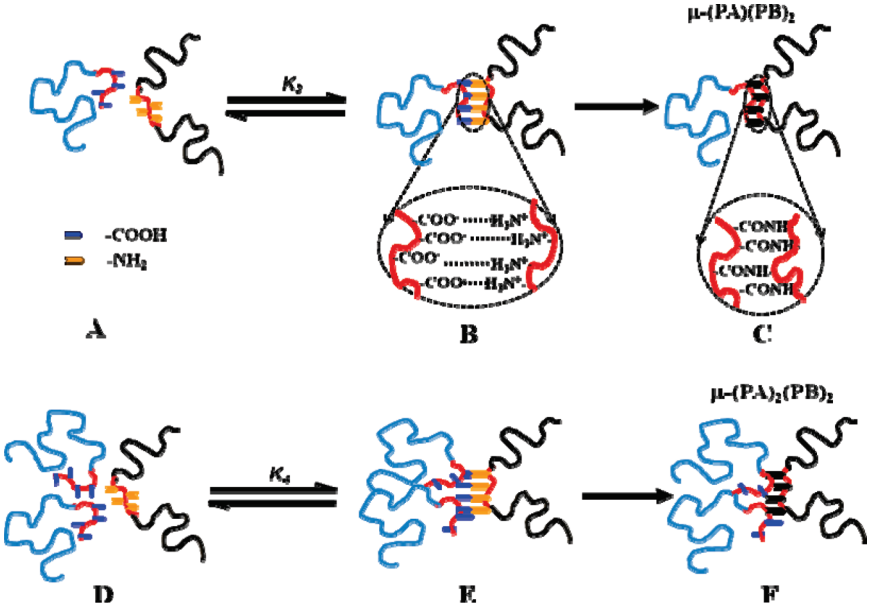


PHNH$_2$



PtBA-*b*-PSCOOH

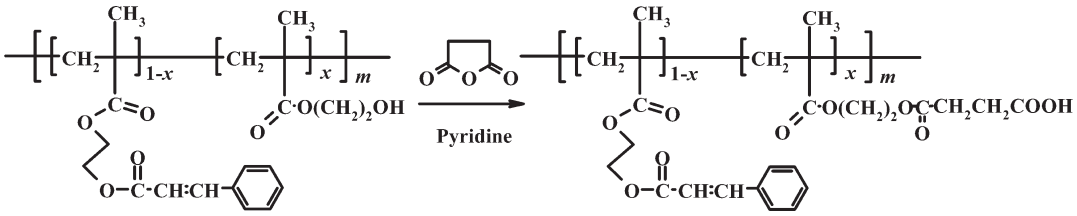
Scheme 2. "Idealized Reaction Mechanism" for Miktoarm Preparation from PtBA-*b*-PSCOOH and PMMA-*b*-PNH$_2$-*b*-PMMA



be linked by CH_3SiCl_3 in order to yield μ-(PA)(PB)(PC). The controlled stoichiometric linkage of the three types of anions requires several steps and is very challenging to execute experimentally, even at room temperature.[22] The aggravated difficulty associated with performing the reactions at low temperatures, such as −78 °C, probably explains why this technique has not been used to prepare μ-(PA)(PB)(PC) systems containing methacrylate or acrylate blocks, which are stable under anionic polymerization conditions only at low temperatures.

One can also prepare arms bearing reactive end groups and then link these different arms together to yield miktoarm star polymers. Click chemistry has, for example, been used to link

Scheme 3. Reaction between HEMA Units and Succinic Anhydride



different polymers.[23−25] Tezuka and co-workers[26] and Kuto and co-workers[27] have prepared polymers with carboxyl and amino end groups. The association and subsequent reaction of these end groups led to the formation of architectural polymers. With the use of only one reactive group per end, the efficiency of the end-linking reaction decreases as the arm length increases. Thus, this approach cannot be used to prepare polymers with long arms. Our method bears close resemblance to this approach. With the use of associating blocks, our methodology can be used to prepare miktoarm copolymers with long arms. The drawback of our strategy is the production of side products that are formed from the reaction of more than two precursory chains.

With the "growing-from" approach, a multifunctional initiator is used.[28−30] The polymerization of different monomers by different mechanisms is performed in sequence. In these cases, controlled radical polymerizations are frequently used. While controlled radical polymerizations are easy to execute, they do not allow preparation of high-molecule arms with low polydispersities, such as those with $M_w/M_n < 1.05$. Also, it is difficult to characterize the individual blocks of a miktoarm copolymer prepared from this approach.

In the "hybrid" approach, the core molecule contains a mixture of terminating and initiating sites. The terminating sites are used to link living polymers, and the initiating sites are used to grow new polymers.[31,32]

II. Experimental Section

Materials. Cinnamoyl chloride (98%), *Z*-glycine (99%), succinic anhydride (99%), hexamethylenediamine (98%), 1,3-dicyclohexylcarbodiimide (99%), trifluoroacetic acid (TFA, 99%), *N*-(3-dimethylaminopropyl)-*N*′-ethyl-carbodiimide hydrochloride (EDCI), 1-hydroxybenzotriazole (HBT), 2-chloro-1-methylpyridinium iodide (CMPI, 97%), tetrabutylammonium bromide (99%), and dimethylformamide (anhydrous, DMF) were purchased from Aldrich and used as received. Pyridine (Fisher Scientific) was refluxed and distilled over CaH_2 under nitrogen. *p*-Toluenesulfonic acid monohydrate (TSA, 98%) was dehydrated at 110 °C under vacuum for 4 h and then was recrystallized in chloroform before using. For the preparation of miktoarm copolymers, triethylamine (TEA, Aldrich, 99.5%) was refluxed in the presence of *p*-toluensulfonyl chloride for 8 h and then distilled. Naphthalene (Aldrich, 99%) was purified by vacuum sublimation. 1,1-Diphenylethylene was distilled over calcium hydride and *n*-butyllithium sequentially. 1,6-Hexamethylenediamine, with one amino group protected by a *tert*-butyloxycarbonyl (BOC) group, i.e. BOC-HEDA, was synthesized following the procedure described by Lee and co-workers.[33]

The precursor for PtBA-*b*-PSCOOH was PtBA-*b*-PHEMA, where PHEMA denotes poly(2-hydroxyethyl methacrylate), which was derived from the hydrolysis of poly(2-trimethylsiloxyethyl methacrylate) or P(HEMA-TMS).[34] To investigate the effect of varying the PtBA block length, three PtBA-*b*-P(HEMA-TMS) samples were prepared by anionic polymerization following procedures reported previously[35] and were then hydrolyzed to yield PtBA-*b*-PHEMA. These were denoted as P1-1, P1-2, and P1-3.

PMMA-*b*-PHEMA-*b*-PMMA. PMMA-*b*-$PHNH_2$-*b*-PMMA and PMMA-*b*-$PGNH_2$-*b*-PMMA were derived from PMMA-*b*-PHEMA-*b*-PMMA. Two PMMA-*b*-P(HEMA-TMS)-*b*-PMMA samples were prepared by anionic polymerization and then hydrolyzed to yield PMMA-*b*-PHEMA-*b*-PMMA. These copolymer samples were denoted as P2-1 and P2-2.

The initiator, lithium naphthalenide, used to prepare PMMA-*b*-P(HEMA-TMS)-*b*-PMMA was synthesized by the reaction of lithium metal (306.6 mg, or 44.2 mmol) with naphthalene (5.1234 g, or 40.0 mmol) in 60.0 mL of dry THF at room temperature for 12 h.[36] Anionic polymerization was performed following standard procedures in THF at −78 °C.[13,37] The diinitiators were prepared *in situ* by reacting lithium naphthalenide with 1,1-diphenylethylene at a molar ratio of 1 to 1.5. HEMA-TMS and MMA were each polymerized for 2.5 h. PMMA-*b*-PHEMA-*b*-PMMA was obtained by the hydrolysis of PMMA-*b*-P(HEMA-TMS)-*b*-PMMA in a solvent mixture of THF/methanol/water (v/v/v = 3/1/0.05). After precipitation into methanol, a white precipitate was obtained in an essentially quantitative yield.

PtBA-*b*-PSCOOH. The preparation of these copolymers invoked partial cinnamation of the PHEMA blocks in P1-1, P1-2, and P1-3 by reaction with cinnamoyl chloride first.[38] The polymers were then reacted with excess succinic anhydride in order to introduce carboxyl groups via Scheme 3.[39] The succinnated copolymers were abbreviated as P1-1-CA30%, P1-1-CA50%, P1-2-CA50%, P1-2-CA70%, and P1-3-CA30%, where CA denotes the carboxyl groups introduced into the PHEMA block, and the number after CA in each code denotes the degree of succination, *x*.

In order to prepare P1-1-CA30%, 1.00 g of P1-1, which contained 0.65 mmol of hydroxyl groups, was dissolved in 3 mL of dry pyridine. To this solution, under vigorous stirring, was then added 0.1067 g (0.64 mmol) of cinnamoyl chloride which was dissolved in 6 mL of dry pyridine. After being stirred at room temperature for 15 h, 0.1 mL of this solution was withdrawn, and the polymer was purified to check the degree of cinnamation ($1 - x$) by ^{1}H NMR. Cinnamoyl chloride addition and the above reaction procedure were repeated until the targeted ($1 - x$) value of 70% was obtained. The resulting product was precipitated in an ice bath and dried under vacuum to yield 0.98 g of PtBA-*b*-(PCEMA-*r*-HEMA). The product was again dissolved in 10 mL of dry pyridine, 1.026 g (10.0 mmol) of succinic anhydride was then added, and the reaction was allowed to proceed at room temperature for 48 h. The complete labeling of the remaining HEMA groups by succinyl groups was confirmed by ^{1}H NMR. The reactant solution was dialyzed against methanol to remove salt or other impurities using a dialysis tubing with a 12 000−14 000 g/mol cutoff molecular weight range. After dialysis, 200 μL of acetic acid was added to neutralize the carboxyl groups before the polymer was precipitated on ice crystals. The white polymer was dried under vacuum to yield 0.90 g of product.

PMMA-*b*-$PHNH_2$-*b*-PMMA. To prepare P2-1-HA30%, 1.00 g of PMMA-*b*-PHEMA-*b*-PMMA was first reacted with cinnamoyl chloride to achieve 70% cinnamation. The residual 30% of the carboxyl groups were reacted with succinic anhydride in order to introduce succinyl groups. The resultant PMMA-*b*-P(CEMA-*r*-COOH)-*b*-PMMA copolymer was purified by precipitation from methanol.

PMMA-*b*-P(CEMA-*r*-COOH)-*b*-PMMA (0.84 g containing 0.16 mmol of carboxyl groups) was dissolved in 7.5 mL of dimethylformamide (DMF). To this solution, under vigorous

stirring and nitrogen bubbling, was then added 0.2248 g of EDCI and 0.1551 g of HBT dissolved in 2.5 mL of DMF. After 15 min, 1.2793 g (6.0 mmol) of BOC-HEDA was added. After 8 h, another 0.2248 g of EDCI and 0.1551 g of HBT in 1.5 mL of DMF were added into the mixture. The reaction was allowed to proceed at room temperature for another 24 h before the solution was centrifuged, and the supernatant was added into 150 mL of methanol in order to precipitate the polymer. After drying under vacuum, 0.82 g of this polymer was obtained.

The polymer was redissolved in 6 mL of chloroform. To this solution were added 3.75 mL of TFA and 0.75 mL of triethylsilane. The reaction was allowed to proceed at room temperature for 12 h. The resulting product was precipitated from methanol. The precipitate was dissolved in 8 mL of THF, which contained 400 μL of triethylamine. This solution was added into methanol to precipitate the polymer again. This procedure was repeated once more before the polymer was dried under vacuum to yield 0.75 g of white solid.

PMMA-*b*-PGNH$_2$-*b*-PMMA. Four samples, including P2-1-Gly30%, P2-1-Gly50%, P2-2-Gly50%, and P2-2-Gly70%, were synthesized. Here, the last number in a sample code denotes the molar fraction of glycinoyl group in the middle block.

To prepare P2-2-Gly70%, 0.50 g of P2-2 (containing 0.28 mmol of hydroxyl groups) was dissolved in 3 mL of dry pyridine. To this solution under vigorous stirring were then added 0.427 g (0.20 mmol) of carbobenzyloxyglycine, 0.0172 g (0.10 mmol) of TSA, and 0.2063 g (1.0 mmol) of DCC dispersed in 2 mL of dry pyridine. After 24 h of stirring at room temperature, 0.1 mL of this solution was withdrawn and purified for glycine labeling density determination. After the desired molar fraction of 70% was reached, the reaction mixture was centrifuged, and the supernatant was added into methanol in order to precipitate the polymer. After dissolution in 4 mL of THF, the polymer solution was added into excess methanol to precipitate the polymer again. This was repeated another time. After drying under vacuum, 0.445 g of product was obtained.

The remaining HEMA groups in 0.445 g of this polymer were reacted with 0.080 g (0.48 mmol) of cinnamoyl chloride in pyridine for 15 h. This reaction mixture was then added into methanol to precipitate the polymer. The polymer was redissolved in 4 mL of THF and added into methanol. This was repeated once again. After the polymer was dried under vacuum, 0.41 g of white product was obtained.

In order to remove the carbobenzyloxy protective groups, the polymer was dissolved in 4 mL of TFA, and the solution was refluxed at 80 °C for 2 h. The TFA was then evaporated under vacuum. The resulting solid was then dissolved in 4 mL of pyridine, and this solution was added into excess methanol to precipitate the polymer. The polymer was subsequently redissolved in THF, and then added into methanol, in order to precipitate the polymer. After drying under vacuum, 0.374 g of P2-2-Gly70% was obtained.

Miktoarm Copolymers. The preparation of miktoarm copolymers was accomplished by the amidization reaction between the carboxyl groups of PtBA-*b*-PSCOOH and the amino groups of PMMA-*b*-PNH$_2$-*b*-PMMA. 2-Chloro-1-methylpyridinium iodide (CMPI) was used as a coupling agent, and triethylamine (TEA) was added to neutralize the HCl and HI molecules generated during the reaction.[27,40] The total concentration of the precursors used in a reaction was normally 0.5 mg/mL, and the molar ratio between the two polymer precursors was 1 unless stated otherwise.

An example of a typical preparation involves first stirring 45 mg (7.4×10^{-4} mmol) of P1-1-CA30% and 55 mg (7.4×10^{-4} mmol) of P2-1-HA30% in 150 mL of dichloromethane for 8 h. The mixture was heated to reflux under N_2 protection. Into this solution were then added 2.3 mg (0.9×10^{-2} mmol) of CMPI and 1.8 mg (1.8×10^{-2} mmol) of TEA dissolved in 50 mL of dichloromethane. The reaction was allowed to proceed for 10 h under stirring, reflux, and N_2 protection before CH_2Cl_2 was removed by rota-evaporation. The solid residue was dissolved in THF and added into excess water to precipitate the copolymer. After drying under vacuum, 98 mg of crude product was obtained for SEC analysis.

In order to follow the reaction, we performed an experiment at a total concentration of 5.0 mg/mL for P1-1-CA30% and P2-1-Gly30%, and samples were taken at the following times: 2 min, 5 min, 10 min, 1 h, 6 h, and 10 h. Immediately after a sample was withdrawn, it was injected into ice water and stirred in order to extract CMPI. SEC analysis indicated that most of miktoarm copolymers were formed within the first hour. Reaction times of >6 h were always used in order to ensure complete reaction.

Miktoarm Copolymer Purification. To remove the residual precursors, 98 mg of the products after carboxyl and amino group reaction were redissolved in THF at 25 mg/mL. Water was then added to induce cloudiness. This cloudy solution was equilibrated in a fridge at 7 °C overnight before being centrifuged at 1500 rpm for 5 min to allow the insoluble components to settle. The supernatant was rotary evaporated to remove solvent, and the precipitate was dried under vacuum. In order to remove the arm precursors completely, the precipitate was purified further following the procedure described above, which was repeated twice. The final yield of the purified product depends on the composition and concentration of arm precursors used in the preparation of miktoarm copolymers. For the specific case of the miktoarm copolymer prepared from P1-1-CA30% and P2-1-HA30% at the total polymer concentration of 0.5 mg/mL, the miktoarm copolymer yield obtained from SEC traces was 51%, and the yield of the purification following the procedures described above was 40%.

Size Exclusion Chromatography and NMR. Size exclusion chromatograph analyses were performed on a system consisting of a 1200 series Agilent isocratic pump, a Wyatt Wish-01 high-pressure injector equipped with a 20 μL loop, a Wyatt DAWN HELEOS-II multiangle laser light scattering (LS) detector (658 nm, 120 mW), and a Wyatt Optilab rEX refractometer (658 nm) or RI detector. The μ-styragel columns used were Waters HT 5, HT 4, and 500 Å. THF was used as the eluant, and its flow rate was 1.00 mL/min. All samples were analyzed at a comparable polymer concentration of 8−10 mg/mL.

To determine the specific refractive index increments (dn_r/dc), the refractive index differences (Δn_r) between a series of polymers and solvent THF were measured using a Wyatt Optilab rEX refractometer. The Δn_r data were then plotted against polymer concentration (c), and the dn_r/dc values were obtained from the slopes of the straight lines.

All ^{1}H NMR measurements were carried out on a Bruker Avance-400 instrument.

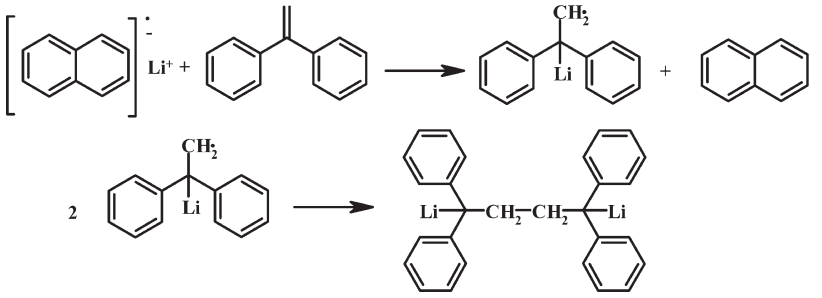
III. Results and Discussion

Precursory Block Copolymers. Three PtBA-*b*-PHEMA samples, P1-1, P1-2, and P1-3, were prepared and derivatized to produce a series of PtBA-*b*-PSCOOH samples. Since the procedure for PtBA-*b*-PSCOOH preparation has been reported previously,[39] it is not repeated here.

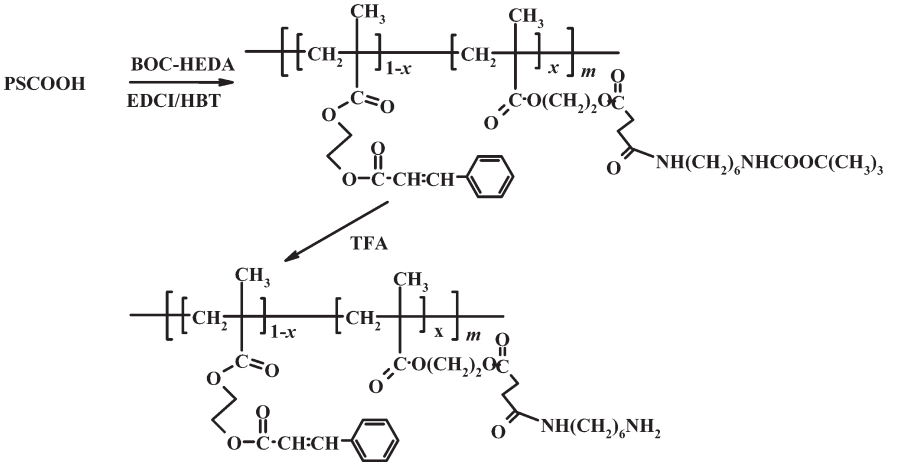
To synthesize PMMA-*b*-P(HEMA-TMS)-*b*-PMMA, the initiator was prepared *in situ* from the reaction between diphenylethylene, a nonhomopolymerizable monomer, and lithium naphthalide (Scheme 4).[32] PMMA-*b*-P(HEMA-TMS)-*b*-PMMA was prepared from the sequential polymerization of HEMA-TMS and MMA. After TMS group removal, two PMMA-*b*-PHEMA-*b*-PMMA samples, P2-1 and P2-2, were produced.

Two methods were used to introduce amino groups into P2-1 and P2-2 in order to investigate the effect of varying the length of the linking group between the polymer backbone and the amino groups. In method 1, the PHEMA block

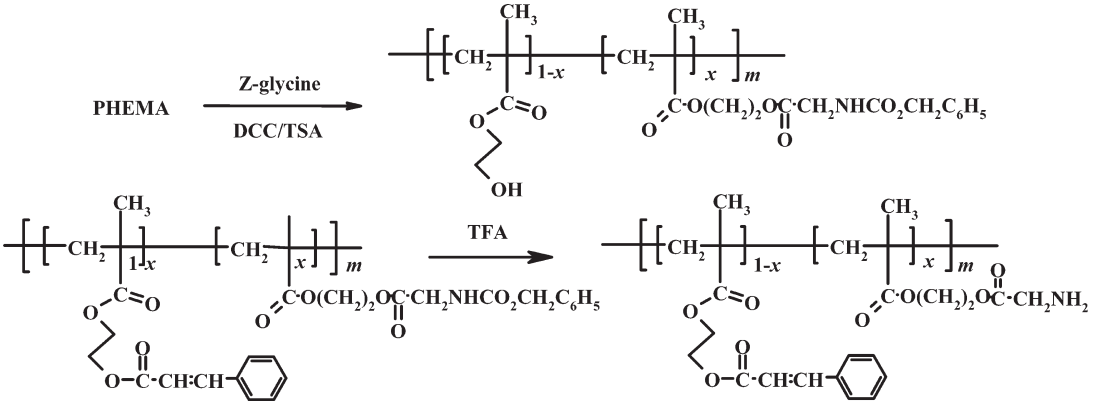
Scheme 4. Reaction for Producing the Diinitiator



Scheme 5. Reactions Used To Attach the Aminohexyl Groups



Scheme 6. Reactions for Obtainining the $PHNH_2$ Block



of P2-1 or P2-2 was partially cinnamated before reaction with excess succinic anhydride to yield PSCOOH, a random block containing 2-cinnamoyloxyethyl methacrylate (CEMA) units and carboxyl groups. The COOH groups were then reacted with excess 6-(BOC-amino)hexylamine (BOC-HEDA). PMMA-*b*-$PHNH_2$-*b*-PMMA with amino groups was obtained after the removal of the protecting BOC group (Scheme 5).

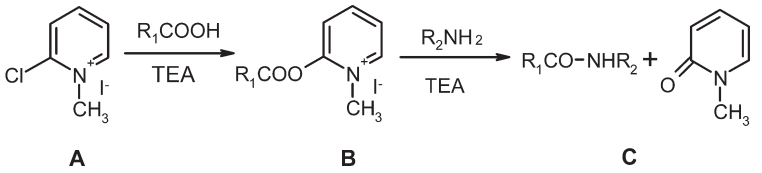
Amino group introduction into P2-1 and P2-2 using method 2 also involved several steps. The PHEMA block was reacted with limiting amounts of *Z*-glycine to yield a random block containing glycine groups and HEMA. The block was then reacted with excess cinnamoyl chloride to yield a random block containing glycine groups and CEMA. The amino-protecting carbobenzyloxy group was removed by treatment with TFA to yield P2-1-Gly*x* or P2-2-Gly*x*, with *x* denoting the molar fraction of glycine-containing units in the $PGNH_2$ blocks. The reaction between PHEMA and *Z*-glycine, and the reaction used for the removal of the benzyloxycarbonyl protecting group, are shown in Scheme 6.

All of the copolymers used were characterized by ^{1}H NMR in order to determine their *n*/*m* ratios and the molar fractions, *x*, of the carboxyl or amino groups in the PCEMA-containing blocks. We have also determined the specific refractive indices, dn_γ/dc, for P1-1-CA30%, P1-2-CA70%, P1-3-CA30%, P2-1-HA30%, and P2-2-Gly70%. Using these dn_γ/dc values, and the SEC system equipped with a RI and LS detector, we determined their weight- and number-average molecular weights, M_w and M_n, respectively (Table 1). Combining the M_n values determined by SEC, with the *n*/*m* values determined

Table 1. Characteristics of the Block Copolymer Precursors Used

sample	dn_γ/dc (mL/g)	SEC $10^{-4}M_n$ (g/mol)	SEC M_w/M_n	NMR n/m	n	m	mx
P1-1-CA30%	0.071	6.1	1.03	11.1/1.0	410	37	11
P1-1-CA50%				11.1/1.0	410	37	19
P1-1-CA60%				11.1/1.0	410	37	22
P1-2-CA50%				11.9/1.0	260	22	11
P1-2-CA70%	0.064	3.9	1.02	11.9/1.0	260	22	15
P1-3-CA30%	0.093	2.7	1.02	2.8/1.0	120	44	13
P2-1-HA30%	0.087	6.9	1.02	6.5/1.0	285	44	13
P2-1-Gly30%				6.5/1.0	285	44	12
P2-1-Gly50%				6.5/1.0	285	44	22
P2-2-Gly50%				8.2/1.0	205	25	12
P2-2-Gly70%	0.089	4.7	1.02	8.2/1.0	205	25	17

Scheme 7. Amidization Reactions Facilitated by the Coupling Agent CMPI



by ^{1}H NMR, the number-average n and m values were calculated and are shown in Table 1. Here n represents the number of repeat units in a PtBA block for polymers of the P1 series and the number of repeats for each PMMA block of the P2 series. The number of carboxyl or amino groups per chain was calculated from mx.

Miktoarm Copolymer Preparation. Miktoarm star copolymer preparation involved two steps. In step 1, PtBA-*b*-PSCOOH and PMMA-*b*-PNH$_2$-*b*-PMMA were equilibrated to allow the establishment of an association equilibrium between the two polymers. Coupling agent was added in step 2 in order to stitch together the associated chains. The carboxyl and amino groups of the block copolymers should associate with one another in the reaction solvent CH_2Cl_2 because this association has previously been demonstrated between acetic acid and triethylamine in $CHCl_3$ and CCl_4.[12] The association between carboxyl and amino groups has already been used for the preparation of various supramolecular structures, including supramolecular block copolymers[41−43] and micelles.[44] In order to facilitate the linkage of the associated chains, an efficient coupling agent, 2-chloro-1-methylpyridinium iodide (CMPI), was used.[40] CMPI facilitates amidization under mild conditions by following the mechanism depicted in Scheme 7. Triethylamine served to neutralize HCl generated from step 1 and HI generated from step 2 of these reactions.

The traces of the SEC refractive index (RI) detector are shown in Figure 1 for P1-1-CA30%, P2-1-HA30%, an equimolar physical mixture of P1-1-CA30% and P2-1-HA30%, and also the crude product obtained from coupling an equimolar mixture of P1-1-CA30% and P2-1-HA30% at a total polymer precursor concentration, c_p, of 0.5 mg/mL. The P1-1-CA30% trace was sharp and symmetric, and the polydispersity index M_w/M_n was 1.03 for this sample. The M_w/M_n value was 1.02 for P2-1-HA30%. The SEC trace of this polymer tailed due to interactions between the amino groups of the polymer and the packing materials of the column. The tailing did not interfere with our accurate determination of the M_w/M_n value because we used a SEC system with both a refractive index and light scattering detectors. These detectors allowed the accurate determination of the molecular weights of the samples independent of the shapes of their SEC traces.

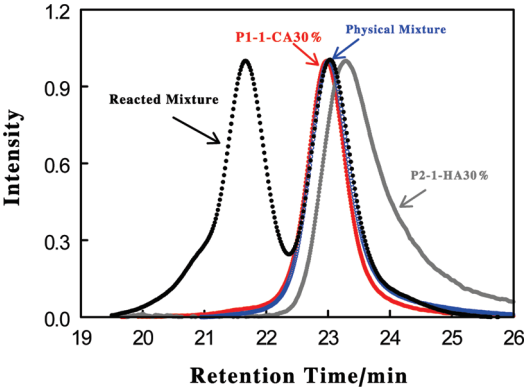


Figure 1. Comparison of SEC RI traces of P1-1-CA30% (red ●), P2-1-HA30% (gray ●), an equimolar physical mixture of P1-1-CA30% and P2-1-HA30% (blue ○), and an amidized equimolar mixture of P1-1-CA30% and P2-1-HA30% (black ●).

The physical mixture of P1-1-CA30% and P2-1-HA30% showed a single narrow SEC trace, with its peak position located between those of P1-1-CA30% and P2-1-HA30%. This behavior was reasonable because the two samples had molecular weights very close to each other, and the superimposition of the peaks of the individual components should generate a peak with its maximum positioned between those of the individual peaks. The SEC peak representing this mixture did not tail, probably due to the fact that the amino groups of P2-1-HA30% were interacting with the carboxyl groups of P1-1-CA30%, and thus the ammonium ions did not interact significantly with the column packing materials.

The SEC trace of the amidized P1-1-CA30% and P2-1-HA30% mixture exhibited two peaks, with one occurring at 21.7 min and the other at 23.1 min. The high-molecular-weight peak exhibited also a small shoulder at 20.9 min. Based on the PS standards, the retention times of 23.1, 21.7, and 20.9 min corresponded to molecular weights of 0.60×10^5, 1.20×10^5, and 1.70×10^5 Da, respectively. These values were comparable with those of 0.60×10^5 Da for P2-1-HA30%, 1.30×10^5 Da for μ-$(PA)_1(PB)_2$, and 1.91×10^5 Da for μ-$(PA)_2(PB)_2$, where PA and PB denote PtBA and PMMA, respectively. These suggested the formation of

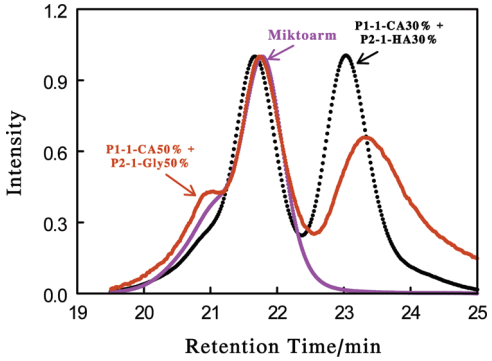


Figure 2. Comparison of SEC traces of an amidized mixture of P1-1-CA50% and P2-1-Gly50% mixture (red ●), an amidized mixture of P1-1-CA30% and P2-1-HA30% (black ●), and a miktoarm copolymer prepared from P1-1-CA30% and P2-1-HA30% after precipitation fractionation (purple ●).

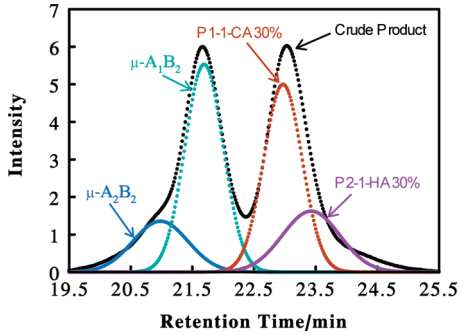


Figure 3. SEC trace of an amidized mixture of P1-1-CA30% and P2-1-HA30% (black ●) and the resolved individual SEC traces for μ-A_1B_2 (green ●), μ-A_2B_2 (blue ●), P1-1-CA30% (brown ●), and P2-1-HA30% (purple ●).

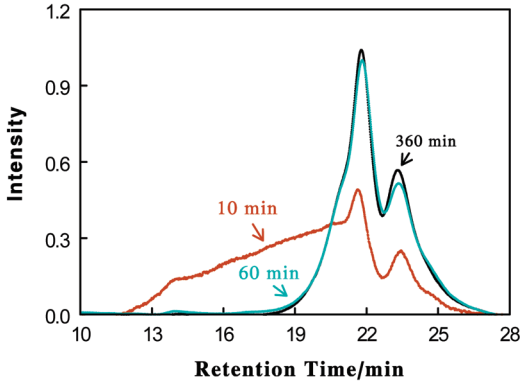


Figure 4. Comparison of SEC traces of a P1-1-CA30% and P2-1-Gly30% reaction mixture at the reaction times of 10 (brown ●), 60 (green ●), and 360 min (black ●).

μ-$(PA)_1(PB)_2$ and μ-$(PA)_2(PB)_2$ miktoarm copolymers from the amidized P1-1-CA30% and P2-1-HA30% precursors.

We have also explored the coupling between P1-1-CA50% and P2-1-Gly50% at $c_p = 0.50$ mg/mL, and the SEC RI trace of the reaction mixture is compared in Figure 2 with that of the P1-1-CA30% and P2-1-HA30% reaction mixture discussed above. The high-molecular-weight peak occurred at 21.8 min, and its shoulder was observed at 20.9 min. Since the shoulder component appeared more abundant in this case, we separated the shoulder and main component of the product by SEC. Our ^{1}H NMR analyses of the resolved components indicated that the tBA-to-MMA molar ratio was 1.0/1.4 for the main component and 1.0/0.70 for the shoulder component. These ratios were consistent with the compositions of μ-$(PtBA_{410})(PMMA_{286})_2$ and μ-$(PtBA_{410})_2$-$(PMMA_{286})_2$, where the numbers in the parentheses denote the number of repeat units for the polymer blocks. The ^{1}H NMR results confirmed unambiguously our production of μ-$(PA)_1(PB)_2$ and μ-$(PA)_2(PB)_2$. Thus, miktoarm copolymers were produced using triblock copolymer precursors containing either the $PHNH_2$ or $PGNH_2$ amino-containing blocks.

Our experiments established that the unreacted block copolymers could be removed by fractional precipitation. Also shown in Figure 2 is the SEC trace of the miktoarm product which had been purified by fractional precipitation of a reaction mixture of P1-1-CA30% and P2-1-HA30%. This fractionation was very successful, and the final combined yield of μ-$(PA)_1(PB)_2$ and μ-$(PA)_2(PB)_2$ was 40%.

We do not know the exact reason for the production of μ-$(PA)_2(PB)_2$ together with μ-$(PA)_1(PB)_2$. It could be due to the mismatch between the number of the carboxyl groups in the P1 chains and that of the amino groups in the P2 chains. It was difficult to produce an exact match between the average numbers of carboxyl and amino groups because the reactions used for attaching the amino and carboxyl groups were not quantitative. Precise quantification of the carboxyl and amino groups by ^{1}H NMR was also difficult due to the low content of these groups. Furthermore, these numbers fluctuate from chain to chain, and thus a mismatch is very likely for any given pair of P1 and P2 chains, even if the average numbers are matched exactly.

The production of a mixture of the μ-$(PA)_2(PB)_2$ and μ-$(PA)_1P(B)_2$ forms of miktoarm copolymers was unfortunate. The presence of the μ-$(PA)_2(PB)_2$ contaminant should not stop the self-assembly of μ-$(PA)_1P(B)_2$ in the solid state or in block-selective solvents. It will only shift the phase diagrams of μ-$(PA)_1P(B)_2$ somewhat. As far as the preparation of materials from the self-assembly of miktoarm copolymers is concerned, the presence of this contaminant is therefore of no consequence.

The SEC traces of the crude products could be resolved using a commercial program, Peakfit, into peaks for μ-$(PA)_1(PB)_2$, μ-$(PA)_2(PB)_2$, and the block copolymer precursors. Figure 3 compares the SEC trace of the crude product from P1-1-CA30% and P2-1-HA30% and the resolved traces of the individual components. The relative areas of the peaks corresponding to μ-$(PA)_1(PB)_2$ and μ-$(PA)_2(PB)_2$ are 13% and 38%, respectively. The total relative area for the reactants was 49%. Ignoring the errors that could derive from the differences in the dn_γ/dc values of the different polymers, we should be able to equate the relative areas of μ-$(PA)_1(PB)_2$ and μ-$(PA)_2(PB)_2$ to their yields. Thus, in this case, the SEC yields for μ-$(PA)_1(PB)_2$ and μ-$(PA)_2(PB)_2$ are 13% and 38%, respectively.

Reaction Progress as a Function of Time. In order to gain insight into the mechanism of miktoarm copolymer formation, we followed the time evolution of product formation from the amidization of P1-1-CA30% and P2-1-Gly30% at $c_p = 5.0$ mg/mL. After the samples were taken, they were quickly injected into icy water to extract the unreacted CMPI. The organic phase was then analyzed by SEC. Figure 4 compares the SEC RI traces of the samples taken at 10 min, 1 h, and 6 h.

At 10 min, the product was not well-defined and contained unknown high-molecular-weight species. The high-molecular-weight impurity was essentially removed at 60 min. No such impurities were detected at the reaction time of 360 min. We also note that the relative height of the peaks of μ-$(PA)_1(PB)_2$ and the precursor mixture did not change with reaction time.

It is unlikely that the amidization reaction was complete by 10 min. Many of the carboxyl groups probably had reacted with CMPI and existed as an intermediate, structure B of Scheme 6. Stirring this sample in icy water caused the coagulation of many of the chains. The indiscriminate reaction between different aggregated chains resulted in the formation of high-molecular-weight impurities during the early stages of the reaction.

By 1 h, the configurations of the associating polymers probably had become locked. This should not be surprising, as a reaction time of 1 h was recommended by Bald et al.[40] We used a reaction time of >6 h to ensure that most of the carboxyl and amino groups had reacted.

The lack of variation between the relative heights of the SEC peaks representing μ-$(PA)_1(PB)_2$ and the precursor mixture with increasing reaction time was not in agreement with predictions of the reaction mechanism shown in Scheme 1. According to this mechanism, the conversion of the physically associated chains into miktoarm chains should deprive the system of the associated clusters. This would shift the association equilibrium to favor association. These sequential reactions should lead to the production of μ-$(PA)_1(PB)_2$ and μ-$(PA)_2(PB)_2$, eventually in quantitative yields.

The constant relative heights of the SEC peaks of μ-$(PA)_1(PB)_2$ and the precursor mixture during the reaction suggests that the association equilibrium between PtBA-*b*-PSCOO and PMMA-*b*-PNH_2-*b*-PMMA was disrupted by the addition of CMPI and triethylamine. This is a reasonable conclusion, as CMPI reacts with the carboxyl groups of PtBA-*b*-PSCOO to generate positively charged intermediates (structure B of Scheme 6). These positively charged intermediates do not associate with PMMA-*b*-PNH_2-*b*-PMMA because they repel the amino-bearing P2 chains. The P2 chains should bear at least some positive charges due to their acceptance of protons from carboxyl groups as well as from HCl and HI which were produced during the amidization reaction. Thus, the yield of the miktoarm product should be determined from the population of the associated chains that existed at the early stages of the reaction, immediately before or after CMPI addition, as was observed experimentally.

Factors Affecting Miktoarm Yields. We have systematically examined the factors that affect the yields of miktoarm formation. In one series of experiments, we reacted P1-1-CA30% with P2-1-Gly30% at different total polymer concentrations (c_p). The variations of the SEC yields of μ-$(PA)_1(PB)_2$ and μ-$(PA)_2(PB)_2$, as well as the total yields of μ-$(PA)_1(PB)_2$ and μ-$(PA)_2(PB)_2$, are plotted as functions of c_p in Figure 5. As c_p increased, the yield of μ-$(PA)_2(PB)_2$, and the total yield of μ-$(PA)_1(PB)_2$ and μ-$(PA)_2(PB)_2$, increased. The yield of μ-$(PA)_1(PB)_2$ increased initially, and subsequently decreased, with increasing c_p.

The total yield of the miktoarm polymer increased with c_p. This was observed because a higher c_p favored, according to Scheme 1, the formation of both the μ-$(PA)_1(PB)_2$ and μ-$(PA)_2(PB)_2$ precursors, which were the associated clusters before chemical stitching. By making the crude assumption that the final concentrations of μ-$(PA)_1(PB)_2$ and μ-$(PA)_2(PB)_2$ produced in a system are proportional to the populations of the μ-$(PA)_1(PB)_2$ and μ-$(PA)_2(PB)_2$ precursors present before CMPI and TEA addition, we have the relationships

$$[\mu\text{-}(PA)_1(PB)_2] \propto K_3[PSOOH]_0[PNH_2]_0 \quad (1)$$

$$[\mu\text{-}(PA)_2(PB)_2] \propto K_4[PSOOH]_0^2[PNH_2]_0 \quad (2)$$

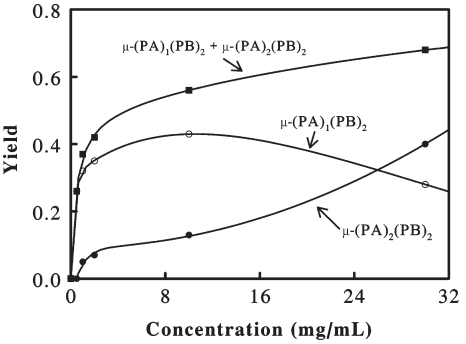


Figure 5. Plots of variation of the yields of μ-$(PA)_1(PB)_2$ (○) and μ-$(PA)_2(PB)_2$ (●), as well as that of μ-$(PA)_1(PB)_2$ and μ-$(PA)_2(PB)_2$ (■), as functions of the total P1-1-CA30% and P2-1-Gly30% concentration (c_p).

Since $[PSOOH]_0$ and $[PNH_2]_0$ are proportional to c_p, $[\mu$-$(PA)_1(PB)_2]$ and $[\mu$-$(PA)_2(PB)_2]$ increase with increasing c_p. This is in agreement with the trend observed when $c_p < 10$ mg/mL.

Evidently

$$[\mu\text{-}(PA)_2(PB)_2]/[\mu\text{-}(PA)_1(PB)_2] \propto [PSCOOH]_0 \quad (3)$$

The relative concentration of μ-A_2B_2 should increase with $[PSOOH]_0$ or c_p, in agreement with the experimental trend.

Equations 2 and 3 cannot explain the decrease of $[\mu$-$(PA)_1(PB)_2]$ at higher values of c_p because these equations were not exactly applicable to our system. The association of small acid and base molecules may have a truly concentration-independent equilibrium constant. For the association of PtBA-*b*-PSCOOH and PMMA-*b*-PNH_2-*b*-PMMA, factors other than the interaction between the carboxyl and amino groups come into play as well. Below the concentration at which the two polymers undergo coil overlapping, K would have contributions from the strength of acid and base interaction and also the steric repulsion between the associating chains. Evidently, this steric repulsion would be stronger among a cluster consisting of two PtBA-*b*-PSCOOH chains and one PMMA-*b*-PNH_2-*b*-PMMA chain than that among a cluster consisting of one PtBA-*b*-PSCOOH chain and one PMMA-*b*-PNH_2-*b*-PMMA chain. Far above the overlapping concentration, the steric repulsion effect may diminish. Thus, K_3 and K_4 should be concentration-dependent, with K_4 showing a greater increase than K_3 with increasing c_p, under otherwise identical conditions.

We also compared the SEC yields of μ-$(PA)_1(PB)_2$ and μ-$(PA)_2(PB)_2$ produced from P1-2-CA50% and P2-2-Gly50% as well as from P1-2-CA70% and P2-2-Gly70% at $c_p = 0.50$ mg/mL. The respective yields of μ-$(PA)_1(PB)_2$ and μ-$(PA)_2(PB)_2$ were 20% and 10% in the former case and 40% and 15% in the latter case. Evidently, the miktoarm product yields increased with mx. This was reasonable because K_3 and K_4 should increase with the average number of carboxyl and amino groups, mx, used for associating the chains.

Decreasing the lengths of the PtBA and PMMA blocks of the precursors should help reduce repulsion between the associating chains and thus increase the K_3 and K_4 values. The SEC yields of μ-$(PA)_1(PB)_2$ and μ-$(PA)_2(PB)_2$ production from P1-3-CA30% and P2-1-HA30% at $c_p = 0.50$ mg/mL were 50% and 23%, respectively. These values changed to 38% and 13%, respectively, when P1-1-CA30% and P2-1-HA30% were used. The main difference between the two sets of polymers was the lengths of their PtBA blocks. The number of repeat units of tBA was 120 in P1-3-CA30%, and 410 in P1-1-CA30%.

We have performed the amidization reaction between polymers containing different numbers of carboxyl and amino groups. For P1-1-CA60% and P2-1-Gly30%, the *mx* values were 22 and 12, respectively. At $c_p = 0.5$ mg/mL, the μ-$(PA)_1(PB)_2$ peak seemed to bear two shoulders on the high-molecular-weight side. While μ-$(PA)_2(PB)_2$ was responsible for one of the shoulders, the one with an even higher molecular weight could be due to μ-$(PA)_1(PB)_4$. From SEC curve deconvolution, we obtained a yield of 35% for μ-$(PA)_1(PB)_2$ and a combined yield of 37% for μ-$(PA)_2(PB)_2$ and μ-$(PA)_1(PB)_4$. When P1-1-CA30% and P2-1-Gly30% were used at $c_p = 0.5$ mg/mL, μ-$(PA)_1(PB)_2$ was produced at a yield of 26% with no noticeable shoulder for the μ-$(PA)_2(PB)_2$. Thus, a mismatch in the *mx* numbers led to the production of one more side product and also a larger amount of the total side products.

IV. Conclusions

Different samples of PtBA-*b*-PSCOOH and PMMA-*b*-PNH_2-*b*-PMMA were prepared and characterized. The carboxyl- and amino-bearing block copolymers associated with each other in dichloromethane to form precursors for μ-$(PA)_1(PB)_2$ and μ-$(PA)_2(PB)_2$. The associated carboxyl and amino groups were then amidized by the addition of CMPI to yield miktoarm copolymers μ-$(PA)_1(PB)_2$ and μ-$(PA)_2(PB)_2$. These miktoarm copolymers could be produced and isolated in decent yields. A systematic study of reaction conditions was conducted, and a number of trends were observed. First, it was found that the amidization reaction proceeded independently of whether PMMA-*b*-P(CEMA-*r*-GNH_2)-*b*-PMMA or PMMA-*b*-P(CEMA-*r*-HNH_2)-*b*-PMMA were used as the amino-bearing block copolymers. Second, only μ-$(PA)_1(PB)_2$ and μ-$(PA)_2(PB)_2$ architectures were produced as the coupled products if the average number of carboxyl and amino groups per coupling chain matched one another. A mismatch in the number in the average number of carboxyl and amino groups per chain could lead to more undesirable products. Third, μ-$(PA)_1(PB)_2$ was produced as the dominant product at low reactant concentrations, and the population of μ-$(PA)_2(PB)_2$ relative to μ-$(PA)_1(PB)_2$ increased as the reactant concentrations increased. Fourthly, the combined yield of μ-$(PA)_1(PB)_2$ and μ-$(PA)_2(PB)_2$ increased with the total reactant concentration. Also, the yields of the miktoarm products increased with decreasing PtBA or PMMA block lengths and increasing numbers of carboxyl and amino groups per chain. All of these trends suggest that whatever factors favored PtBA-*b*-PSCOOH and PMMA-*b*-PNH_2-*b*-PMMA association helped increase the yields of the miktoarm products.

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