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Tailor-made compositional gradient copolymer by many-shot RAFT emulsion polymerization method

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A many-shot RAFT emulsion polymerization method is proposed to synthesize gradient copolymers with high molecular weight and tailor-made compositional gradient. In this method each shot consisting of comonomers with pre-set different fractions and targeting the molecular weight of 10,000 g/mol was added in stepwise manner during the reaction. High conversions over 95% were achieved in 35min after each shot. The compositional variation along the polymer chain was then directly determined by the comonomer fractions added at each shot. Styrene/n-butyl acrylate gradient copolymers (including linear and V-shaped gradient) with molecular weights as high as 90,000 g/mol were prepared by this method. The composition profiles along polymer chains agreed well with theoretical prediction and the composition distribution among polymer chains was narrow. The gradient copolymers showed different thermal, phase separation and properties from their block counterparts as expected. These results demonstrated the successful tailor-making of the gradient copolymer. The current strategy will be a facile method to prepare the tailor-made gradient copolymer with high molecular weight and within short time.

Introduction

The property of copolymer is not only determined by its monomer type and composition but also strongly associated with its chain sequence, i.e. the distribution of different monomer units along the polymer chain. For an A-B binary system, for example, the A-B diblock and A-B-A triblock copolymers always have totally different properties compared with the random A-co-B copolymer even their composition fractions are the same.[1,2] Recently, with the development of synthesis techniques copolymers with more sophisticated chain structures have received great attentions.[3-6] Besides block copolymer which possesses sharp transitions at the conjunction of different blocks, gradient copolymers have intrigued great interests recently.[7-9] Gradient copolymer was defined as a type of copolymer, the composition of which continuously varies from head to tail of polymer chains. Even in well-defined gradient copolymer, the local monomer sequence is not able to be exactly defined. What the composition gradient describes is a long-range composition changing trend. It is no sense to define a very local monomer composition in a single chain of the gradient copolymer. Also, it is impossible to define unambiguous compositional gradient of an individual chain[7]. Instead, the ensemble average of the local composition should be defined as the average over all the polymer chains at a specific position X. As reported by Broadbelt et.al in their theoretical simulations[10], the local monomer sequences are still quite disperse even if the molecular masses were relatively uniform. The continuous composition change along the polymer chains leads to the formation of many separate microphase domains with different compositions in the gradient copolymer, as supported by the theoretical simulations and experimental data.[11-13] This special morphology brings gradient copolymers unique properties and potentials in novel applications such as phase stabilizers[14], vibration-damping materials[15] and recently reported multi-shape memory materials[16].

To synthesize gradient copolymers, living/controlled polymerization techniques must be employed, i.e. anionic polymerization, cationic polymerization, ring-opening metathesis polymerization as well as controlled/living radical polymerization (CLRP) techniques such as NMP (nitroxide mediated polymerization)[17], ATRP (atom transfer radical polymerization)[18] and RAFT (reversible addition-fragmentation chain transfer radical polymerization)[19]. In recent years, CLRPs have been employed to prepare a great variety of gradient copolymers due to their applicability to almost all vinyl monomers and tolerance with water and impurities. As a matter of fact, most batch CLRPs give spontaneous gradient copolymers due to the different reactivity ratios. For a certain monomer pair and given composition, only one kind of gradient that is determined by the reactivity ratios can form. Many examples have been reported in different monomer pairs[7,8], e.g. styrene/acrylic acid[20], tert-butyl acrylate/octadecyl methacrylate[21], styrene/methyl methacrylate[22] and n-butyl acrylate/n-butyl methacrylate[23] etc. To tune the composition gradient more flexibly, a semi-batch approach has been developed. With this method, part of the monomer is continuously added into the reaction system during the reaction so as to change the instantaneous comonomer ratios. The monomer feeding rate could be constant or changed with time. For example, Torkelson et al. reported many studies with this method by NMP[13,24], such as styrene/n-butyl methacrylate, styrene/n- or t-butyl acrylate and styrene/4-vinylpyridine. Billon et al. also reported different systems by RAFT[25] and NMP[26]. In such cases the composition gradient is still unknown in advance and need to be inferred from structure characterizations. To tailor-make the compositional gradient, a model-based approach has been developed. Mathematic models have been utilized to predict the kinetics and determine the feeding policies according to the targeted gradient composition in order to prepare a precisely controlled gradient structure, as examples reported by NMP[27], RAFT[28,29] and ATRP[30,31]. In these model-based methods detailed kinetic studies need to be carried out in advance to predict the instantaneous monomer concentrations and design appropriate feeding policy.

So far, the molecular weight of the most gradient copolymers synthesized by CLRP was quite low. However, high molecular weight is particularly important to gradient copolymers. The special properties of the gradient copolymer largely rely on the formation of microphase separation giving many separate domains with different compositions. Low molecular weight might form a homogeneous system without micro-phase separation.

Most gradient copolymers prepared by CLRPs were carried out by solution polymerization. In these cases the concentration of radicals should be kept at a low level in order to suppress the irreversible terminations avoiding the generation of large amount of dead chains, so the reaction rate was lowered simultaneously. When the target molecular weight was as high as about 50,000 g/mol, the polymerization rate could be very low, which limits the increase of the molecular weight. In our earlier model-based trial preparing the gradient copolymer of styrene/n-butyl acrylate, the reaction time was as long as 50 hours even though the molecular weight was set at only 30,000g/mol to avoid serious termination[28]. Zhou et al. prepared the methyl methacrylate/2-hydroxyethyl methacrylate gradient copolymer by model-based ATRP in solution[31]. 50,000g/mol was reached after 7-hour polymerization at 90^{o}C, and the conversion was still very low in the end. Matyjaszewski et al.[32] also reported the preparation of forced gradient by miniemulsion polymerization, but they still suffered from low molecular weight and relatively slow polymerization rate. 3 hours were consumed for the copolymerization of butyl methacrylate and methyl methacrylate, but only the molecular weight of 12,000g/mol was reached. Higher molecular weights were obtained by NMP with higher polymerization temperature. Torkelson et al.[13] reported the synthesis of styrene/n-butyl acrylate gradient copolymers with molecular weight as high as 96,900 g/mol. The reaction time was 6 to 9 hours. In Billon's study[26], the forced styrene/n-butyl acrylate gradient copolymer prepared by NMP in solution cost 5 hours and reached the molecular weight of 40,000g/mol. These attempts in solution NMP were all carried out at high operating temperature (i.e.120^{o}C) in order to achieve higher polymerization rate, which could be serious limitation in some cases.

Compared to homogeneous polymerization techniques, emulsion polymerization facilitates suppression on irreversible radical termination and thus shortens the reaction time in the preparation of high molecular weight polymers through the radical segregation effect.[33,34] In our current work, many-shot RAFT emulsion polymerization is proposed for the first time to prepare the tailor-made gradient copolymer with high molecular weight within a short time.

Many-shot Synthetic Strategy to Prepare Tailor-Made Gradient Copolymer

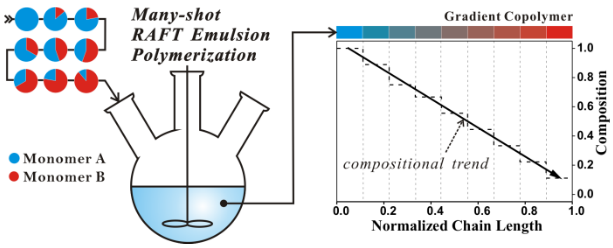
So far the gradient copolymers with tailor-made chain sequence could only be synthesized via model-based semi-batch method.[7,8] For example, monomer A was first all put into the reactor, then monomer B was added in a programmed continuous manner during the reaction. The B's feeding rate was determined by calculating the consumption of A according to the deigned gradient. So it requires a full understanding of kinetics in order to predict the instantaneous monomer concentrations.

RAFT emulsion polymerization is one of the most intensively studied fields, but the early attempts in ab initio RAFT emulsion were perplexed by many problems such as poor control on molecular weight and coagulum formation[35-37]. Most recently, these problems have been solved[38-42]. For example, by precisely tuning the structure of a macro-RAFT agent, which served as both surfactant and chain transfer agent, well-controlled manner over polystyrene and even poly(styrene-b-n-butyl acrylate-b-styrene) triblock copolymers had been achieved.[43] It was demonstrated that RAFT emulsion polymerization not only gave a good control over molecular weight and molecular weight distribution but also proceeded very fast which led to a low dead chain fraction in the products even with molecular weight higher than 100,000 kg/mol. The fast polymerization rate and easily controllable feature enlightened us with a convenient method to prepare gradient copolymers with high molecular weight.

Different from homogenous system, i.e. solution or bulk polymerization, emulsion polymerization has a more complicated mechanism including component distribution and migration, and it's sharply sensitive to experimental conditions.[34] It is well known that the apparent reactivity ratios in an emulsion copolymerization system could be different from those of their homogeneous counterparts. Especially when

RAFT is involved, it becomes frustratingly complicated for accurate kinetic modelling for the whole process.[44]

Considering that the compositional gradient actually deals with the long range compositional changing trend and the local composition deviation is less important, we propose a many-shot feeding policy to synthesize gradient copolymer by RAFT emulsion polymerization so that kinetic model is not necessary. As illustrated in Scheme 1, a polymer chain is divided into many segmental blocks and the average composition of each block will be continuously changed from one chain end to the other. Monomer mixtures of A&B will be added by many shots. Monomer composition of each shot will be continuously changed according to the designed copolymer composition. After each shot the polymerization is allowed to proceed to very high monomer conversion. So, the average composition of the resulted block will be equal to the added monomer composition of the corresponding shot even though the composition might drift within the block. It should be noted that the heterogeneous nature of emulsion polymerization and reactivity ratios might change the compositional profile within the block but it will have little influence on the average composition of the block since the monomer conversion is controlled to be very high. In the end of the polymerization, a kind of "many-block" copolymer will be obtained. Since the shooting monomer composition is continuously changed according to the designed copolymer composition and the number of blocks is high, the resulted many-block copolymer could be considered as the designed compositional gradient copolymer, where the long range compositional profile is more relevant than the local monomer sequence.



Scheme 1. Illustration of the many-shot RAFT emulsion polymerization strategy to manipulate gradient structure

Very recently, Perrier et al. demonstrated the synthesis of decablock polymers via multiple addition of the same monomer by RAFT solution polymerization.[45] The dead chain fraction was very low. We noticed that the monomer employed was acrylamide, which has very high propagation rate constants (k_p). Actually, in the cases of monomers with lower k_p like styrene, it was expected by simulation that the dead chain fraction would dramatically increase at very high conversion in each stage when the polymerization was carried out in the homogeneous polymerization process.[46] In the current strategy, the problem was solved by taking advantage of the segregation effect of radicals in the emulsion polymerization, which significantly suppresses the irreversible termination reactons.[33,34]

Experimental Section

Materials. Styrene (St) was purified by vacuum distillation, and n-butyl acrylate (nBA) was washed with sodium hydroxide aqueous solution (5 wt %) to remove the inhibitors. Potassium persulfate (KPS,>99%), hydrochloric acid (HCl, 37 wt%) and sodium hydroxide (NaOH, >96%) were used as received. The poly(acrylic acid)$_{20}$-b-polystyrene$_5$ trithiocarbonate macroRAFT agent was synthesized following the method described elsewhere[43]. The structure was confirmed by GPC with a molecular weight of 2,300g/mol and ^{1}H NMR with a structure of Poly(Acrylic Acid$_{20}$-b-Styrene$_5$).

Synthesis of Poly(St-b-nBA) Diblock Copolymer (DI). 1.15g macroRAFT agent was dissolved in 70g deionized water. Then 25g styrene was mixed with the solution in a 250ml flask. After 30min deoxygenating by nitrogen purge, the water bath was set at 70^{o}C. Then, 0.0270g KPS dissolved in 3g water was injected to start the reaction. After 45min, 0.1g NaOH dissolved in 27g deionized water was injected by syringe at a rate of 3ml/min. 105 minutes later, 20g nBA was injected at 3ml/min by syringe to start the second period. The polymerization of nBA last 55min until the reaction was completed. Samples were withdrawn during the process for gravimetric, GPC and ^{1}H NMR analysis. After the reaction, the latex was slowly decanted into 2 wt% HCl solution to coagulate the colloidal. The product was then filtered and dried.

Synthesis of Poly(St-b-nBA-b-St) Triblock Copolymer (TRI). 1.15g macroRAFT agent was dissolved in 70g deionized water. Then 12.5g styrene was mixed with the solution in a 250ml flask. After 30min deoxygenating by nitrogen purge, the water bath was set at 70^{o}C. Then, 0.0270g KPS dissolved in 3g water was injected to start the reaction. After 45min, 0.1g NaOH dissolved in 27g deionized water was injected by syringe at a rate of 3ml/min. 55 minutes later, 20g nBA was injected at 3ml/min by syringe to start the second period. The polymerization of nBA last 55min. After that, another 12.5g styrene was injected into the emulsion at 3ml/min. 60 minutes later, the reaction was completed. Samples were withdrawn during the process for gravimetric, GPC and NMR analysis. After the reaction, the latex was slowly decanted into 2 wt% HCl solution to coagulate the colloidal. The product was then filtered and dried.

Synthesis of Poly(St-co-nBA) random Copolymer (RAN). 1.15g macroRAFT agent was dissolved in 70g deionized water. Then 7.5g styrene and 6g nBA were mixed with the solution in a 250ml flask. After 30min deoxygenating by nitrogen purge, the water bath was set at 70^{o}C. Then, 0.0270g KPS dissolved in 3g water was injected to start the reaction. After 30 min, 0.1g NaOH dissolved in 27g deionized water was injected by syringe at a rate of 3ml/min. 15 minutes later, a mixture composed of 17.5g styrene and 14g nBA was injected at a rate of 0.5ml/min by syringe pump for about 60min. Then total reaction time was 180min. Samples were withdrawn during the process for gravimetric, GPC and ^{1}H NMR analysis. After the reaction, the latex was slowly decanted into 2 wt% HCl solution to coagulate the colloidal. The product was then filtered and dried. Here, we didn't put all the monomer into the system at once because if we directly add them all, it would be very easy to cause colloidal coagulation. A semi-batch method which firstly polymerized a small seed and then added NaOH would help solve this problem[40].

Synthesis of Poly(St-grad-nBA) Linear Gradient Copolymer (LG). 2.3g macroRAFT agent was dissolved in 150g deionized water. Then 10g styrene was mixed with the solution in a 500ml flask. After 30min deoxygenating by nitrogen purge, the water bath was set at 70^{o}C. Then, 0.0540g KPS dissolved in 3g water was injected to start the reaction. After 45min, 0.2g NaOH dissolved in 47g deionized water was injected by syringe at a rate of 3ml/min. The first period lasted for 80min, followed by 8 times monomer addition operations. The monomer composition varied sequentially according to Table 1a with a constant weight of 10g. The reaction time was set to acquire high conversions for each period. Samples were withdrawn during the process for gravimetric, GPC and ^{1}H NMR analysis. After the reaction, the latex was slowly decanted into 2 wt% HCl solution to coagulate the colloidal. The product was then filtered and dried.

Synthesis of Poly(St-grad-nBA-grad-St) V-shaped Gradient Copolymer (VG). 2.3g macro-RAFT agent was dissolved in 150g deionized water. Then 10g styrene was mixed with the solution in a 500ml flask. During 30min deoxygenating by nitrogen purge, the water bath was set at 70^{o}C. Then, 0.0540g KPS dissolved in 3g water was injected to start the reaction. After 45min, 0.2g NaOH dissolved in 47g deionized water was injected by syringe at a rate of 3ml/min. The first period lasted for 80min, followed by 8 times monomer addition operations. The monomer composition varied sequentially according to Table 1b. The reaction time was set to acquire abundant conversions for each period. Samples were withdrawn during the process for gravimetric, GPC and NMR analysis. After the reaction, the latex was slowly decanted into 2 wt% HCl solution to coagulate the colloidal. The product was then filtered and dried. The Poly(St-grad-MA-grad-St) was also prepared in the identical way except replacing nBA with MA. Without special remarks, all the VG refers to Poly(St-grad-nBA-grad-St).

Table 1. Feed policy of the LG and VG copolymers

a) Linear gradient copolymer

No.	Styrene weight/g[a]	Reaction time/min	Conversion of each step
L-1	10	80	96.4%
L-2	8.8	35	95.9%
L-3	7.7	35	96.5%
L-4	6.6	35	95.6%
L-5	5.5	35	95.9%
L-6	4.4	35	96.2%
L-7	3.3	35	95.5%
L-8	2.2	35	95.9%
L-9	1.1	35	96.5%

b) V-shaped gradient copolymer

No.	Styrene weight/g[a]	Reaction time/min	Conversion of each step
V-1	10	80	95.0%
V-2	7.5	35	94.4%
V-3	5.0	35	95.0%
V-4	2.5	35	98.7%
V-5	0.0	35	97.4%
V-6	2.5	35	94.5%
V-7	5.0	35	95.2%
V-8	7.5	35	95.9%
V-9	10	35	97.2%

[a] The total amount of monomer per shot is 10g.

GPC Characterization. Number-average molecular weight (M_n), weight-average molecular weight (M_w), and PDI (M_w/M_n) were measured by gel permeation chromatography (Waters 1525 binary HPLC pump, Waters 2414 refractive index detector, Waters717 autosampler). The molecular weight and PDI were derived from a calibration curve based on narrow polystyrene standards.

GPEC Characterization. Gradient polymer elution chromatography was utilized to experimentally investigate the compositional distribution of all the polymer chains. The experiments were performed with an Agilent 1100 series systems. The column was a Kromasil silica gel column (100Å, 150*4.6mm, 5μm, scienhome Science Instruments Co., Ltd. Tianjin, China). The applied solvents were HPLC grade dichloromethane (DCM) and acetonitrile (ACN). The linear gradient used was changed from 100%DCM to 70%DCM+30%ACN in 9 min. The detailed operation was referred to *ref* 47, which proved to be effective for the polystyrene and polyacrylate systems. All the signals were recorded by a UV detector at 311 nm. Due to the incorporation of carboxylic acid groups by the macro-RAFT agent(21 –COOH per chain), which might be strongly absorbed to columns and disturb the result, all the samples were modified by methylation process according to *ref* 48.

DSC Characterization. Differential Scanning Calorimetry (DSC) experiments were conducted on a TA Q200 (TA Instruments) to determine the T_g of different polymers. Temperature range was from -90°C to 150°C with heating and cooling rate of 10°C/min after a waiting period of 2min at 150°C to eliminate the thermal history.

NMR Analysis. Compositions of different copolymers were determined by ^{1}H NMR using acetone as solvent on a BRUKER DMX 500 MHz spectrometer. The signal at 0.9ppm

(3H, $-CH_3$ at the end of butyl group) was used for nBA and 7.13ppm (5H, -Ph from styrene) was used for styrene, respectively. The ratios of two kinds of monomers in the polymer chain were thus calculated.

AFM Observation. Samples were prepared by spin coating the 2wt% tetrahydrofuran solution of corresponding polymers onto a silicon wafer twice in order to diminish the interaction between wafer and polymers, and then annealed at 130°C for 12 hours. Images were obtained from the Scanning Probe Microscopy (Veeco, MultiMode) in tapping mode.

Results and Discussion

Preparation of Gradient Copolymers. As illustrated in Table 1a, nine shots of mixed-monomers with preset compositions were added in sequence after the former one reached high conversion. Here, we set the block numbers to be nine. It’s a compromise between the structure requirements and experiment’s convenience. The styrene’s content was decreased gradually in each shot until almost pure PnBA was obtained at the chain end. The average composition along the polymer chains would follow the long-range gradient variation trend, which was preset.

Benefiting from the facility of this method to adjust chain compositional profiles, the gradient structure was further altered from linear gradient to V-shaped gradient. V-shaped gradient copolymer, which differs from the general one that possesses a gradually varied composition from A-rich segment to B-rich segment, has a monomeric profile from A-rich to B-rich then reverting back to A-rich. This idea originated from the styrene-butadiene-styrene triblock copolymer (SBS) that has been widely used as thermalplastic elastomer. The PS capped at both ends of a chain serves as physical cross-linking points, so the properties of SBS can be greatly enhanced compared with the SB diblock.

As summarized in Table 1-2 and Figure 1-2, two kinds of gradient copolymers, linear gradient (LG) and V-shaped gradient (VG), were successfully synthesized. Conversions, molecular weights, PDIs and compositions at the end of each segment were monitored. Table 1 shows high conversions (>95%) were achieved after each shot during the process. 35 minutes are enough to polymerize 10,000g/mol here and reach 95% conversion, which is impossible for solution or bulk CLRPs with the same concentration ratio of initiator to RAFT agent. It took 80 minutes to reach high monomer conversion for the first shot polymerization owing to the nucleation period. Table 2 shows the good correlations between theoretic molecular weight and experimental Mn from GPC measurements. The PDIs are around 1.50. The relative PDIs might be too high if it was in a RAFT solution or bulk polymerization but is acceptable in a RAFT emulsion polymerization, especially for such a high molecular weight.[13,36,43,49,50] Figure 1 gives the corresponding GPC curves. The molecular weight distribution curves move to higher molecular weight as a whole, which clearly demonstrates the living nature of the polymer chain during the whole process. This molecular weight information demonstrates a good control over the polymerizations. Figure 2 shows the agreement of the gradient composition change between theoretical values and ^1H NMR measurements in both cases.

Table 2. GPC results of LG and VG copolymers

a) Linear gradient copolymer

No.	Total reaction time/min	Theoretic M_n/g mol^{-1}	The GPC Mn/g mol^{-1}
L-1	80	12k	14k
L-3	150	31k	44k
L-5	220	50k	58k
L-7	290	70k	75k
L-9	360	89k	89k

b) V-shaped gradient copolymer

No.	Total reaction time/min	Theoretic M_n/g mol^{-1}	The GPC Mn/g mol^{-1}
V-1	80	11k	14k
V-3	150	30k	35k
V-5	220	49k	56k
V-7	290	68k	73k
V-9	360	89k	90k

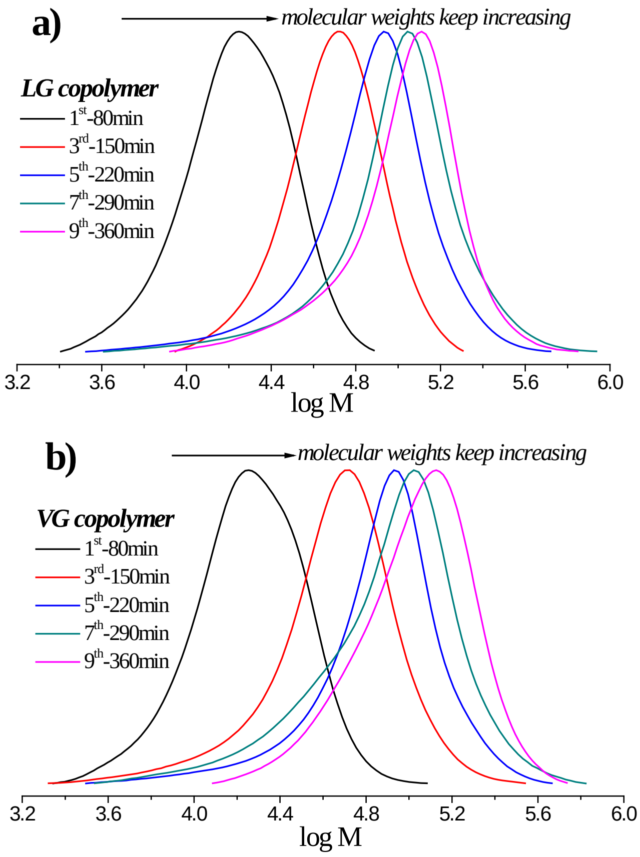


Figure 1. GPC chromatograms of the gradient copolymers during the reaction. a) LG; b) VG.

The composition distributions of the final gradient copolymers were characterized by gradient polymer elution chromatography (GPEC) according to *ref* 47. UV signals at 311nm from thioester groups were recorded. The results are presented in Figure 3. For comparison, GPEC was also run for homopolymers PSt (Mn=90k, PDI=1.29) and PBA (Mn=100k, PDI=1.68) prepared with the same method (macro-RAFT mediated emulsion polymerization). As seen in Figure 3, PSt-peak appears at 2~3min and PBA-peak around 8~9min, respectively. It suggests that the elution time is highly sensitive to the composition of BA and St in polymers for the current GPEC method. The peaks of the gradient copolymers, LG and VG, eluted out at 6~7 min just between those of PSt and PBA as expected. It is interesting to see that the bandwidths of the peaks of LG and VG gradient copolymers are quite narrow, suggesting the composition distribution is very narrow as well. At the first thought, the result conflicted with the well-accepted notion that the copolymer composition could be very broad in the emulsion polymerization due to monomer transportation in Stage I and II. Actually, in the current case, the whole process was divided into nine steps. At the beginning of each step, a monomer mixture with preset composition was shot and then the polymerization was allowed to proceed to very high monomer conversion (>95%). Thus, the compositional drifting was limited within each step. Furthermore, the radical segregation effect strongly suppressed the termination, leading to a high livingness in the end of the whole polymerization as we will discuss later. These features enable most of polymer chains experience almost the same growth kinetics except the short particle nucleation period in the first step of the polymerization. That is why the composition distribution is so narrow.

The slight variance between LG and VG is caused by the higher St content in LG, in accordance with the ^{1}H NMR results. Here it should be noted that although methylation processes were carried out to eliminate the effect of carboxylic acid groups from the macro-RAFT agent, they seem hard to be totally converted. The possible absorption effect might disturb the elution, even in the homopolymers. As a result, rather skewed elution curves were observed.

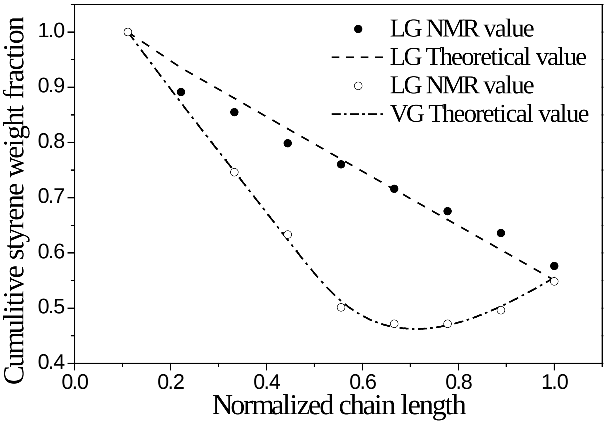


Figure 2. Cumulative compositions of styrene wt% in LG&VG copolymers determined by ^{1}H NMR

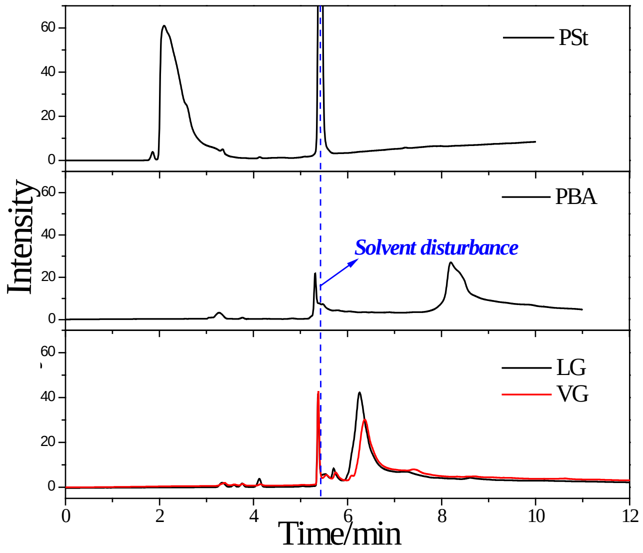


Figure 3. GPEC curves of Polystyrene (PSt), Poly(n-butyl acrylate) (PBA), linear gradient (LG) and V-shaped gradient (VG) copolymer. The linear gradient solvent used was changed from 100% DCM to 70 %DCM +30%ACN in 9min.

The key for the synthesis of polymer with high molecular weight via CLRP is to minimize the dead chain fraction while the polymerization time remains reasonable. If we set n_D as the number of dead chains, n_D should follows eq.1 as

$$n_D = \int_0^t k_t [R\cdot]^2 dt ......(eq.1)$$

where k_t is the termination factor, $[R\cdot]$ is the radical concentration, and t is the reaction time, respectively. It is obvious that n_D is positively related with the reaction time *t*. In all the CLRPs, $[R\cdot]$ was kept at a relatively stable low level in order to suppress the irreversible termination, leading to a long reaction time. In our previous report[51], the gradient copolymer synthesized in solution with only 15,000g/mol and 70% conversion required 35 hours, and the dead chain percent was calculated to be around 20%. In the current case, 35 minutes were enough to polymerize 10,000g/mol onto the polymer chain and 6 hours were sufficient to prepare 90,000g/mol macromolecule even at 70°C. As for the dead chain mole fractions (f_D), it can be roughly estimated by eq.2 (chain transfer to solvent, monomer or polymer is assumed to be negligible here). If we assume all the radicals generated from initiators ended as dead chains, the maximum dead chain fraction would be

$$f_D = \frac{\alpha f [KPS]_0 (1-e^{-k_d t})}{[RAFT]_0 + \alpha f [KPS]_0 (1-e^{-k_d t})} ......(eq.2)$$

where $[RAFT]_0$ is the initial RAFT concentration, $[KPS]_0$ is the initial KPS concentration, *f* is the initiator efficiency factor, *t* is the polymerization time, and k_d is the dissociation rate of initiator, respectively. *a* is set as 1 for combination termination or set as 2 for the disproportionation termination. The longer the reaction time was, the more initiator decomposed, so f_D would be greater. Here we set a=2(in total disproportionation termination case, while styrene mainly follows combination termination) to estimate the maximum f_D. k_d and f are set as $4.31\cdot10^{-5}(s^{-1})$[52] and 0.5[53], respectively. For the gradient copolymer prepared in 360 minutes by current method, the theoretical maximum f_D is 10.8%, not to mention the actual amount.

Preparation of Random, Diblock and Triblock Copolymers.

Different from the complexity in preparing gradient copolymers, the synthesis of random and block ones has been fully developed.[43] Table 3 and Table 4 give the corresponding characterizations which can be used to verify the structures, including composition from ^{1}H NMR and molecular weight and distributions from GPC. All the characterizations fit the theoretical structures we designed.

Table 3. Molecular information of random, diblock and triblock copolymers

Type	Segment	Reaction Time/min	Conv.	Theoretic M_n/ g mol^{-1}	The GPC M_n/ g mol^{-1}	PDI
RAN	P(St-co-nBA)	180	95.0%	86k	90k	1.43
DI	PS	160	97.5%	51k	54k	1.54
	PS-b-PnBA	60	96.9%	89k	91k	1.58
TRI	PS	115	95.3%	26k	27k	1.34
	PS-b-PnBA	55	96.2%	64k	68k	1.60
	PS-b-PnBA-b-PS	70	97.1%	89k	94k	1.55

Table 4. Compositions determined by ^{1}H NMR for all the copolymers

Styrene content	RAN	DI	TRI	LG	VG
Weight%	55.8%	56.9%	57.0%	57.4%	54.9%
Mole%	60.8%	61.9%	62.0%	62.4%	60.0%
Volume%[a]	56.5%	57.5%	57.7%	58.1%	55.6%

[a] Volume fractions were calculated with densities of 1.05g cm-3 for PS and 1.08g cm-3 for PnBA.

Thermal Properties and Phase Separation Behaviours.

Glass transition temperatures (T_g) were measured by DSC for the gradient copolymers and block copolymers. As illustrated in Figure 4a, obviously discrete transitions at around -50°C and 100°C can be viewed from diblock and triblock copolymers, which indicates the distinct phase separations in block copolymer systems. However, both LG and VG possess very broad and continuous transitions from nearly -50°C to 100°C. These transitions are more obvious in the derivative curves of heat flow[13] in Figure 4b. The T_g curves are exactly the same as the gradient copolymers produced by model-based solution polymerization method with continuously monomer-adding manner in our previous work[28], which demonstrates the gradient copolymer prepared by the current method has similar microphase separation behaviour as the gradient copolymer from the model-based methods.

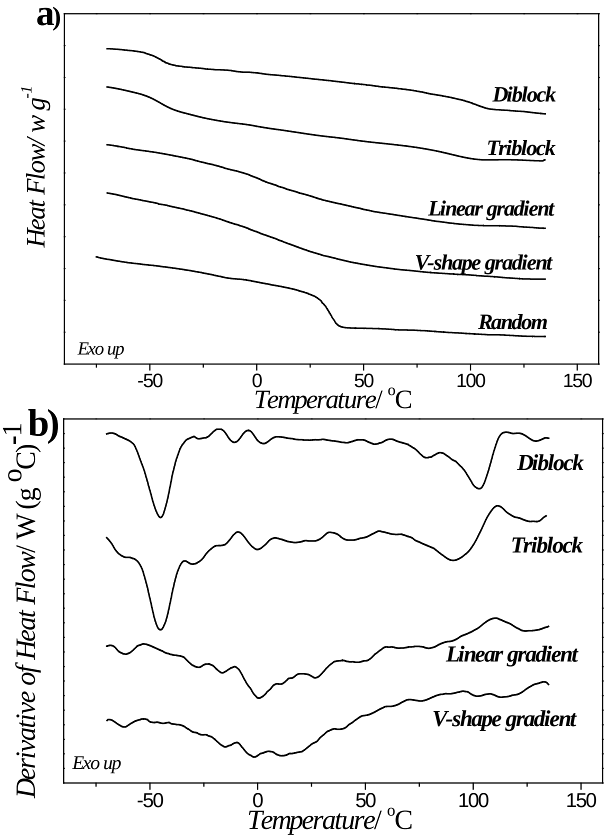


Figure 4. T_g of five kinds of copolymers determined by DSC

AFM was carried out for direct observation of the microphase separations of the gradient copolymers. Extensively theoretical simulations have been performed on the phase separation of gradient copolymers.[11,54] The results suggested that a lamellar morphology would be formed, and there should be a gradual composition transition from one microphase to another. But to our best knowledge, direct observation of gradient copolymers' microphase separation was still rare.[26,55]

AFM images of the gradient, diblock, and triblock copolymers with similar compositions are exhibited in Figure 5. The two block copolymers show clear boundaries between the yellow and red domains. In the LG and VG systems, much weaker phase separations were found. Especially, there're no evident or sharp boundaries between the yellow and red domains. Instead, vague and gradual transitions, i.e. intermediate colours, from the red to yellow can be clearly viewed. Different colours represent different microphase domains that consist of different compositions. For a long time, the simulations have revealed the intermediate transitional phase should exist in the gradient copolymers, but persuasively experimental observation is still in lack. Figure 5 clearly demonstrate the transitions between different microphases. As for the shape of the morphology, it looks like worm-like or twisted lamellar structures. In addition, Figure 5f gives the cross-sectional curves of the four copolymers, showing the phase contrast as a function of the distance referred to some point. It is obvious that two block copolymers exhibited much steeper compositional transitions than the gradient ones.

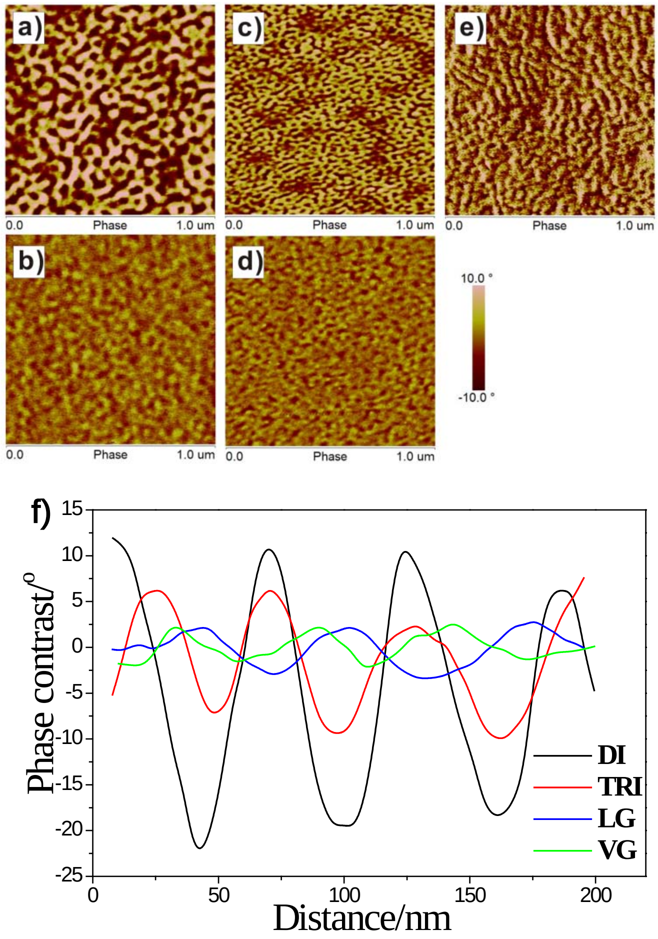


Figure 5. AFM phase images of the St/nBA-copolymers: a) DI; b) LG; c) TRI; d) VG; e) St/MA V-shaped gradient copolymers. f) periodic phase contrast as a function of distance from some referred points, derived from the AFM images a&b&c&d

Styrene and n-butyl acrylate belong to a moderately segregating system with intermediate Flory-Huggins interaction parameter χ[13]. To further verify the AFM observations on the gradient copolymer, we also examined the St/MA system which should show strong phase separation capacity[16]. Poly(St-co-MA) V-shaped gradient copolymer was synthesized by just replacing nBA with MA. As illustrated in Figure 5e, lamellae-like phase morphology was indeed obtained as the theoretical models have predicted. This MA-based gradient copolymer displays more obvious gradient transitions between the red and yellow domains.

Conclusions

In conclusion, many-shot RAFT emulsion polymerization strategy proved to be a facile method to prepare gradient copolymer with high molecular weight. The fast polymerization rate of RAFT emulsion polymerization is the key point of this method. It enabled the polymerization with a targeted molecular weight of 10,000 g/mol reach high conversion of over 95% in 35 minutes in current work. Fast polymerization rate is essential for the employing of many-shot feeding policy and avoiding the formation of large fraction of dead chains. It also enables the achievement of high molecular weight at a relatively low polymerization temperature and short time. Compared with the model-based method, this method avoids the complicated investigations over various kinetic, diffusion parameters etc. These all make the current method a convenient but robust one to prepare copolymers with tailor-made composition gradients.

For the first time the special microphase separation behaviour of gradient copolymers was observed clearly by AFM method. Gradual transitions between different microphases can be viewed directly.

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1 Matyjaszewski, K. *Science* 2011, **333**, 1104.
2 Palermo, E. F.; McNeil, A. J. *Macromolecules* 2012, **45**, 5948.
3 Hermel, T. J.; Hahn, S. F.; Chaffin, K. A.; Gerberich, W. W.; Bates, F. S. *Macromolecules* 2003, **36**, 2190.
4 Wieberger, F.; Neuber, C.; Ober, C. K.; Schmidt, H.-W. *Adv. Mater.* 2012, **24**, 5939.
5 Matyjaszewski, K.; Tsarevsky, N. V. *Nat. Chem.* 2009, **1**, 276.
6 Hentschel, J.; Kushner, A. M.; Ziller, J.; Guan, Z. B. *Angew. Chem. Int. Ed.* 2012, **51**, 10561.
7 Beginn, U. *Colloid. Polym. Sci.* 2008, **286**, 1465.
8 Zaremski, M. Y.; Kalugin, D. I.; Golubev, V. B. *Polym. Sci. Ser. A* 2009, **51**, 103.
9 Matyjaszewski, K.; Ziegler, M. J.; Arehart, S. V.; Greszta, D.; Pakula, T. *J. Phys. Org. Chem.* 2000, **13**, 775.
10 Wang, L.; Broadbelt, L. J. *Macromolecules* 2009, **42**, 7961.
11 Jiang, R.; Jin, Q.; Li, B.; Ding, D.; Wickham, R. A.; Shi, A.-C. *Macromolecules* 2008, **41**, 5457.
12 Slimani, M. Z.; Moreno, A. J.; Rossi, G.; Colmenero, J. *Macromolecules* 2013, **46**, 5066.
13 Mok, M. M.; Kim, J.; Wong, C. L. H.; Marrou, S. R.; Woo, D. J.; Dettmer, C. M.; Nguyen, S. T.; Ellison, C. J.; Shull, K. R.; Torkelson, J. M. *Macromolecules* 2009, **42**, 7863.
14 Kim, J.; Gray, M. K.; Zhou, H. Y.; Nguyen, S. T.; Torkelson, J. M. *Macromolecules* 2005, **38**, 1037.
15 Hashimoto, T.; Tsukahara, Y.; Tachi, K.; Kawai, H. *Macromolecules* 1983, **16**, 648.

16 Luo, Y.; Guo, Y.; Gao, X.; Li, B.-G.; Xie, T. *Adv. Mater.* 2013, **25**, 743.

17 Grubbs, R. B. *Polym. Rev.* 2011, **51**, 104.

18 Matyjaszewski, K.; Xia, J. H. *Chem. Rev.* 2001, **101**, 2921.

19 Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* 2005, **58**, 379.

20 Lefay, C.; Charleux, B.; Save, M.; Chassenieux, C.; Guerret, O.; Magnet, S. *Polymer* 2006, **47**, 1935.

21 Qin, S.; Saget, J.; Pyun, J.; Jia, S.; Kowalewski, T. *Macromolecules* 2003, **36**, 8969.

22 Luo, Y.; Liu, X. *J. Polym. Sci., Part A: Polym. Chem.* 2004, **42**, 6248.

23 Min, K.; Li, M.; Matyjaszewski, K. *J. Polym. Sci., Part A: Polym. Chem.* 2005, **43**, 3616.

24 Mok, M. M.; Ellison, C. J.; Torkelson, J. M. *Macromolecules* 2011, **44**, 6220.

25 Escalé, P.; Ting, S. R. S.; Khoukh, A.; Rubatat, L.; Save, M.; Stenzel, M. H.; Billon, L. *Macromolecules* 2011, **44**, 5911.

26 Karaky, K.; Pere, E.; Pouchan, C.; Desbrieres, J.; Derail, C.; Billon, L. *Soft Matter* 2006, **2**, 770.

27 Wang, L.; Broadbelt, L. J. *Macromolecules* 2009, **42**, 8118.

28 Sun, X.; Luo, Y.; Wang, R.; Li, B.-G.; Zhu, S. *AIChE J.* 2008, **54**, 1073.

29 Ye, Y. S.; Schork, F. J. *Ind. Eng. Chem. Res.* 2009, **48**, 10827.

30 Zhao, Y.; Luo, Y. W.; Ye, C. H.; Li, B. G.; Zhu, S. P. *J. Polym. Sci., Part A: Polym. Chem.* 2009, **47**, 69.

31 Zhou, Y. N.; Li, J. J.; Luo, Z. H. *J. Polym. Sci., Part A: Polym. Chem.* 2012, **50**, 3052.

32 Min, K.; Kwon Oh, J.; Matyjaszewski, K. *J. Polym. Sci., Part A: Polym. Chem.* 2007, **45**, 1413.

33 Zetterlund, P. B.; Kagawa, Y.; Okubo, M., *Chem. Rev.* 2008, **108**, 3747-3794.

34 Chern, C. S. *Prog. Polym. Sci.* 2006, **31**, 443.

35 Cunningham, M. F. *Prog. Polym. Sci.* 2008, **33**, 365.

36 Monteiro, M. J.; Hodgson, M.; De Brouwer, H. *J. Polym. Sci., Part A: Polym. Chem.* 2000, **38**, 3864.

37 Uzulina, I.; Kanagasabapathy, S.; Claverie, *J. Macromol. Symp.* 2000, **150**, 33.

38 Ferguson, C. J.; Hughes, R. J.; Pham, B. T.; Hawkett, B. S.; Gilbert, R. G.; Serelis, A. K.; Such, C. H. *Macromolecules* 2002, **35**, 9243.

39 Ferguson, C. J.; Hughes, R. J.; Nguyen, D.; Pham, B. T. T.; Gilbert, R. G.; Serelis, A. K.; Such, C. H.; Hawkett, B. S. *Macromolecules* 2005, **38**, 2191.

40 Wang, X. G.; Luo, Y. W.; Li, B. G.; Zhu, S. P. *Macromolecules* 2009, **42**, 6414.

41 Urbani, C. N.; Monteiro, M. J. *Macromolecules* 2009, **42**, 3884.

42 Zhang, W. J.; D'Agosto, F.; Boyron, O.; Rieger, J.; Charleux, B. *Macromolecules* 2011, **44**, 7584.

43 Luo, Y. W.; Wang, X. G.; Zhu, Y.; Li, B. G.; Zhu, S. P. *Macromolecules* 2010, **43**, 7472.

44 Prescott, S. W.; Ballard, M. J.; Rizzardo, E.; Gilbert, R. G. *Aust. J. Chem.* 2002, **55**, 415.

45 Gody, G.; Maschmeyer, T.; Zetterlund, P. B.; Perrier, S., *Macromolecules* 2014. DOI:10.1021/ma402286e

46 Wang, A. R.; Zhu, S., J. Polym. Sci. Part A: Polym. Chem. 2003, **41**, 1553-1566.

47 Guo, R.; Shi, Z.; Wang, X.; Dong, A.; Zhang, J. *Polym. Chem.* 2012, **3**, 1314.

48 Couvreur, L.; Lefay, C.; Belleney, J.; Charleux, B.; Guerret, O.; Magnet, S. *Macromolecules* 2003, **36**, 8260.

49 Chenal, M.; Bouteiller, L.; Rieger, J. *Polym. Chem.* 2013, **4**, 752-762.

50 Rieger, J.; Zhang, W.; Stoffelbach, F. O.; Charleux, B. *Macromolecules* 2010, **43**, 6302-6310.

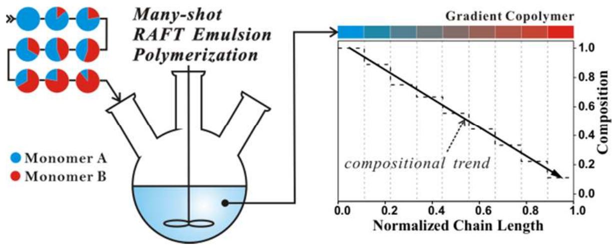
51 Sun, X.; Luo, Y.; Wang, R.; Li, B.-G.; Liu, B.; Zhu, S. *Macromolecules* 2007, **40**, 849.

52 Santos, A. M.; Vindevoghel, P.; Graillat, C.; Guyot, A.; Guillot, J. *J. Polym. Sci., Part A: Polym. Chem.* 1996, **34**, 1271.

53 Gilbert, R. G., *Emulsion polymerization: a mechanistic approach.* Academic Press: London, 1995.

54 Wang, R.; Li, W.; Luo, Y.; Li, B.-G.; Shi, A.-C.; Zhu, S. *Macromolecules* 2009, **42**, 2275.

55 Mok, M. M.; Pujari, S.; Burghardt, W. R.; Dettmer, C. M.; Nguyen, S. T.; Ellison, C. J.; Torkelson, J. M. *Macromolecules* 2008, **41**, 5818.



A many-shot RAFT emulsion polymerization method to synthesize gradient copolymers with high molecular weight and tailor-made compositional gradient