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Branched methyl methacrylate copolymer particles prepared by RAFT dispersion polymerization

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Abstract Reversible addition–fragmentation chain transfer (RAFT) dispersion copolymerization of methyl methacrylate (MMA) and tripropylene glycol diacrylate (TPGDA) was carried out in ethanol/water in the present work. S-1-Dodecyl-S′-(α,α-dimethyl-α″-aceticacid) trithiocarbonate (TTC) was used as a chain transfer agent to inhibit the occurrence of gelation. Branched poly(methyl methacrylate) (PMMA) particles with a very narrow size distribution was prepared by a two-stage method: the addition of a RAFT agent and a TPGDA agent to the system followed the nucleation stage. The particles had an average diameter within 1.9–2.7 μm and size distribution of 1.12–1.24. Molecular weight, molecular weight distribution, compositions and structure of copolymer were investigated by GPC and 1H NMR characterization. The GPC curves showed a bimodal distribution, indicating that MMA homopolymer was synthesised during the nucleation stage. In addition, 1H-NMR proved that MMA and TPGDA branched copolymer was synthesised after the nucleation stage. TPGDA fraction in the copolymer was lower than that in the initial monomer. It was determined that the intrinsic viscosity of the copolymer decreased with conversion and the Mark–Houwink exponent α of copolymer was reduced from 0.643 to 0.548, which further confirmed the branched structure of the copolymer.

Keywords RAFT polymerization · Dispersion polymerization · Branched polymer

Introduction

"Living" controlled radical polymerization has been a powerful technique to synthesize well-defined structure polymer by controlling molecular weight,

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molecular weight distribution and tailored architecture. Three “living” radical polymerization techniques which are receiving more and more attention in academia are nitroxide-mediated radical polymerization (NMP) [1], atom transfer radical polymerization (ATRP) [2], and reversible addition–fragmentation chain transfer (RAFT) polymerization [3]. RAFT polymerization was considered as one of the most promising controlled free radical polymerization due to its compatibility with a wide range of monomers and its versatility.

Dispersion polymerization is a versatile method of preparing micron and submicron particles with a narrow size distribution which have many applications in coatings, electronics, and information technology and support materials for biochemcals. Size control and size uniformity are key factors for their applications. In recent years, “living” radical polymerization has been extended to dispersion polymerization, which include NMP dispersion polymerization [4, 5], RAFT dispersion photopolymerization [6], RAFT dispersion polymerization [7–9], and ATRP dispersion polymerization [10, 11]. There are many benefits of combining “living” radical polymerization with dispersion polymerization. First, it can produce microspheres of uniform size. Second, molecular weight and molecular weight distribution of the polymer can be controlled. Third, the chain-end of polymer is living, which can be modified by postpolymerization. However, it has caused the issue of particle size becoming out of control when combining “living” radical polymerization with dispersion polymerization. Although controlled molecular weight and living chain-end were obtained, particle size distribution was very broad [4, 5, 10]. Furthermore, it was found that particle size uniformity and colloidal stability declined when more RAFT agents were introduced to the system [7, 8].

Recent years have witnessed an increase in interest into the synthesization of hyperbranched polymers. Hyperbranched polymers have some properties similar to dendrimers, such as high numbers of functional groups on their surface, excellent solubility in a vast range of solvents, and very low viscosity, which make them applicable for resin modification, encapsulation, pharmaceutical use and catalysis. There are many methods to synthesize hyperbranched polymers, in which step-growth polymerization via polycondensation of ABx monomers is the most common one. Here, A and B are the two functionalities that can react with each other but not with themselves. Frechet et al. first discovered self-condensing vinyl polymerization (SCVP) [12–14], which uses a vinyl monomer that has a second functional group capable of initiating the polymerization of other groups. In addition, group transfer polymerization (GTP) [15] and ATRP [16, 17] were also used for the preparation of hyperbranched polymers. In 2000, Sherrington’s group reported a facile and cost-effective way to synthesize branched polymers from vinyl monomers [18]. Their strategy involves a multifunctional vinyl comonomer and mercaptan in the conventional free radical polymerization of a vinyl monomer. The multifunctional vinyl comonomer acts as a cross-linking agent to generate branches while the mercaptan as a chain transfer agent to prevent gel formation. With the correct balance of these two reagents, a soluble branched polymer can be obtained. They copolymerized methyl methacrylate with different multifunctional comonomers containing from two to six acrylate functional groups and synthesised a variety of soluble, branched architectures [19]. After then, the strategy has been extended to "living" radical polymerization, including GTP [20], ATRP [21] and RAFT polymerization [22–24].

In our previous research [25], we studied the free radical polymerization in the presence of trithiocarbonate (TTC), and found that polymerization demonstrated controlled/living characteristics. In this paper, we investigate the use of RAFT technique to produce branched polymer in a two-stage dispersion polymerization. We employed TPGDA as a multifunctional vinyl comonomer and TTC as a chain transfer agent to inhibit gelation. The particles with branched architecture were successfully produced in dispersion polymerization. The copolymers were studied via NMR and GPC. As far as we know, TTC has never been used to produce branched polymer in a dispersion free radical polymerizations.

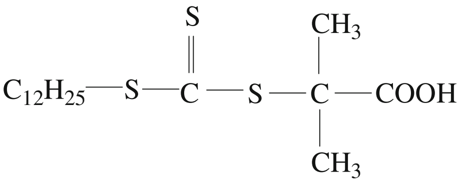
Experimental section

Materials

Methanol, ethanol and poly (N-vinylpyrrolidone) (PVP, K30, average Mw ~10,000) were used without further purification. Methyl methacrylate (MMA, 99%) and tripropylene glycol diacrylate (TPGDA, industrial grade) were passed through an activated basic alumina column to remove radical inhibitors and stored at 0–5 °C before use. 2, 2′-Azobisisobutylronitrile (AIBN) was recrystallized from ethanol. S-1-Dodecyl-S′-(α,α′-dimethyl-α″-aceticacid) trithiocarbonate (seen Fig. 1) was synthesised as reported earlier [26].

Postaddition dispersion polymerization

Detailed recipes are listed in Table 1, run 2–6. A 100 mL three-neck round bottom flask equipped with a magnetic stirrer, a condenser, a thermometer and a gas inlet was charged with ethanol, water, MMA, stabilizer PVP, and initiator AIBN. The resultant homogeneous solution was deoxygenated by bubbling nitrogen gas at room temperature for at least 20 min and then the flask was immersed in a 70 °C oil bath. When the solution reached polymerization temperature, it began to account. The TTC dissolved in the ethanol was added into the system after the solution became turbidity (about 5 min after reaction started).



$$C_{12}H_{25}-S-\overset{\overset{S}{\|}}{C}-S-\overset{CH_3}{\underset{CH_3}{C}}-COOH$$

Fig. 1 Structure of S-1-dodecyl-S′-(α, α′-dimethyl-α″-aceticacid) trithioncarbonate

Table 1 Recipe for the RAFT dispersion polymerizations of MMA

Run	Part one					Part two[a]				
	EtOH (g)	H_2O (g)	MMA (g)	AIBN (g)	PVP (wt%)[b]	EtOH (g)	H_2O (g)	MMA (g)	RAFT (mol%)[b]	TPGDA (mol%)[b]
1	10	10	2	0.02	12					
2	10	10	2	0.02	12	2			0.27	
3	10	10	2	0.02	12	2			0.55	
4[c]	10	10	2	0.02	12	2			0.82	
5	10	10	2	0.02	20	2			1.1	
6	10	10	2	0.02	25	2			2.0	
7	10	10	2	0.04	12	10	10	2	1.7	1.7
8	10	10	2	0.04	12	10	10	2	1.7	4.4
9	10	10	2	0.04	30	10	10	2	1.7	1.7
10	10	10	2	0.04	30	10	10	2	1.7	4.4

[a] Part two ingredients were added 5 min after reaction started (run 2–6); 40 min after reaction started (run 7–10)

[b] Based on MMA

[c] Coagulum formed due to poor colloidal stability

Two stage dispersion polymerization

Detailed recipes are listed in Table 1, run 7–10. Different from postaddition dispersion polymerization, all the stabilizer PVP, initiator AIBN and half of MMA, water and ethanol were added to the reaction flask. After bubbling nitrogen for 20 min, the flask was immersed in a 70 °C oil bath. Time began to account when the solution reached the polymerization temperature. TTC and comonomer TPGDA were dissolved in the remaining MMA, ethanol and water solvent at 70 °C under nitrogen. After the polymerization reaction ran for 40 min, the preheated solution was added into the reaction flask. During the polymerization, aliquots were withdrawn from the reaction at different time intervals. The resulting latex particles were centrifuged and redispersed in methanol ten times to ensure the removal of any excess stabilizer and unreacted monomer. The final particles were dried in a vacuum oven at 50 °C over night for further characterization.

Characterizations

Monomer conversion was measured gravimetrically. Molecular weight and molecular weight distribution (MWD) were determined on an Agilent HP 1100 GPC equipped with two Pl gel column, monodisperse polystyrene standards as the calibration. THF was the mobile phase, the column oven temperature was set to 30 °C and the flow rate was 1 mL/min. The samples were prepared for injection by dissolving 20 mg of polymer in 4 mL of HPLC grade THF; 20 µl of this mixture was then injected and data collected for 20 min. The interferometer refractometer, RID A, was employed to carry out the d*n*/d*c* measurements in an off-line mode of operation. The Agilent HP 1100 GPC package for Windows was used to collect and process the signals transmitted from the detectors to the computer and to produce the molar mass distribution and molar mass versus elution volume plots. ^{1}H NMR spectra were recorded on a 400 MHz Bruker UltraShield spectrometer using CDCl3 as the solvent and tetramethylsilane as the reference. The viscosity measurements of polymer in toluene were performed with an Ubbelohde viscometer at 25 °C. Optical microscope (Leica DMLP) was used to study the morphology of the synthesised PMMA particles. The number-average diameters (D_n), weight-average diameters (D_w) and size distribution PDI (D_w/D_n) were obtained by counting 500 individual particles from the optical microscope photographs with the following formulas:

$$D_n = \sum_{i=1}^{n} d_i / n \tag{1}$$

$$D_w = \sum_{i=1}^{n} d_i^4 \bigg/ \sum_{i=1}^{n} d_i^3 \tag{2}$$

$$PDI = D_w / D_n \tag{3}$$

Results and discussions

Dispersion homopolymerization in the presence of TTC

Choe et al. [8] studied dispersion polymerization of styrene in an ethanol medium under the regulation of RAFT agent. They dissolved RAFT agent in the ethanol and added them after nucleation (solution became turbidity), which they called “the postaddition of RAFT”. We carried out postaddition dispersion polymerization of MMA in the presence of five concentrations of RAFT (0.27, 0.55, 0.82, 1.1and 2.0 mol% of RAFT based on MMA) following the work of Choe and co-workers. The recipes are presented in Table 1(run 2–6 in Table 1). For the reactions with 0.27 and 0.55 mol% RAFT, latex with good colloidal stability was produced. With a higher RAFT content (0.82 mol%), a pink coagulant at the bottom of the reactor was observed until the end of the reaction. This demonstrated particle size uniformity and colloidal stability decline when more RAFT agents are introduced same as the results of Choe et al. [8]. Colloidal stability was improved when increasing stabilizer concentration in dispersion polymerization (run 4–6 in Table 1).

It is well known that rate retardation is associated with RAFT polymerization [27]. However, rate retardation does not appear in the dispersion polymerization of MMA under the regulation of TTC. In contrast, polymerization rate increases when the amount of TTC increases (seen in Fig. 2). This could be related to the surfactant structure of TTC (seen in Fig. 1, TTC has a hydrophobic dodecyl group and a hydrophilic carboxyl group). Because of this structure TTC can serve as a surfactant to accelerate monomer transport to the growing radicals that enhanced smaller size particles.

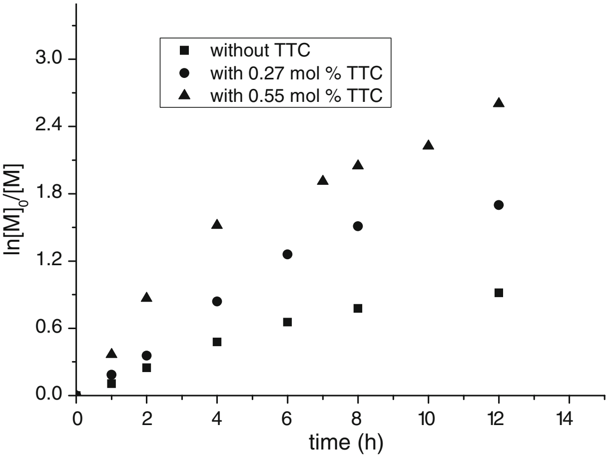


Fig. 2 Polymerization kinetics for the dispersion polymerization of MMA without TTC (*filled square*), with 0.27 mol% TTC (*filled circle*) and 0.55 mol% TTC (*filled triangle*) by postaddition in an ethanol medium at 70 °C, 12wt% PVP

Two stage dispersion copolymerization to produce copolymer microsphere

A number of authors have shown that the addition of multifunctional monomer (MFM) may result in flocculation or coagulation of the product, odd-shaped particles, a broad size distribution and a lack of control over the dispersion reaction [28–30]. Two stage dispersion polymerization was successfully employed to solve the problem of coagulum and particle size control resulting from addition of TPGDA and RAFT agent. The morphology of the microspheres was studied by an optical microscope. Optical microscope photos of methacrylate copolymer microsphere are present in Fig. 3. The variations of particle size of methacrylate copolymer microsphere synthesised by two stage dispersion polymerization are shown in Fig. 4. In general, Dn increased with polymerization time and size distribution was in the range of 1.1–1.3. In the same level of stabilizer concentration 30wt% (run 9 and 10), microspheres prepared at higher mole ratio of TPGDA/MMA had a bigger particle size. This is because copolymer synthesised at higher mole ratio of TPGDA/MMA had higher extent of branching, which resulted in a bigger microsphere size. Moreover the polymeric stabilizer plays an important role in the dispersion polymerization for preparing monodisperse particles. The particles prepared at 12wt% PVP concentration (run 7) were bigger than those at 30wt% (run 9) because a large number of stabilizing molecules induced a large surface area that reduces the surface energy. This is also the behavior observed in the conventional dispersion polymerization.

As seen in Fig. 5, when 30wt% PVP (run 9 and 10) is used, polymerization rate is higher and the conversion reached to 0.84 and 0.82 at 12 h. Again, when 12wt% of PVP (run 7 and 8) is used, the conversion of 0.63 and 0.57 is obtained at 12 h. It has been demonstrated that the nuclei is always the major location for polymerization in particle growth stage; both polymerization rate and conversion increased due to an increased number of nuclei formed when increasing the PVP concentration.

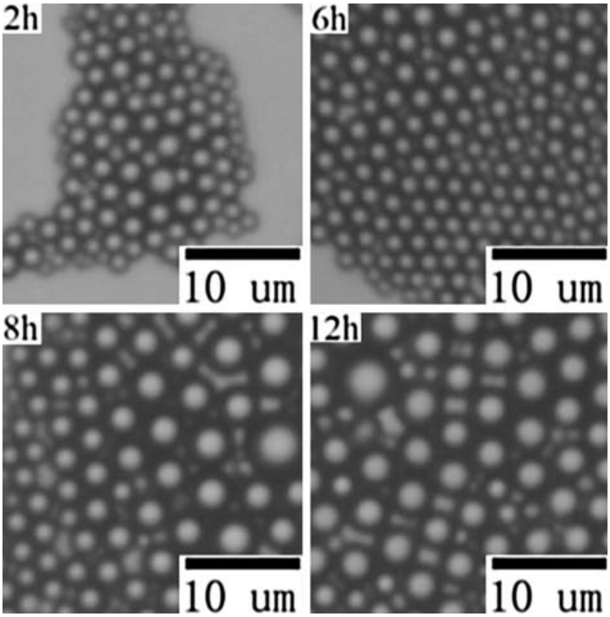


Fig. 3 Photomicrographs of methacrylate copolymer (run 7 in Table 1) microsphere at different time

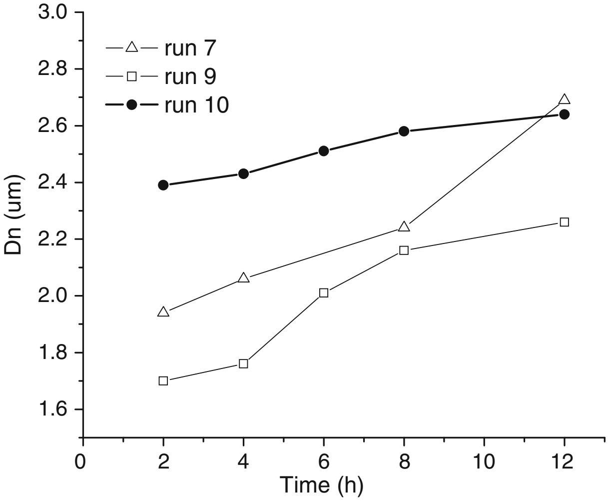


Fig. 4 The number-average diameters (Dn) of branched copolymer microsphere versus time for the two-stage method in ethanol–water mixture (10/10, w/w)

The structures of methacrylate copolymer

The mechanism of branched copolymer formation from the copolymerization of multifunctional vinyl monomer (MFM) and MMA has been proposed in an early

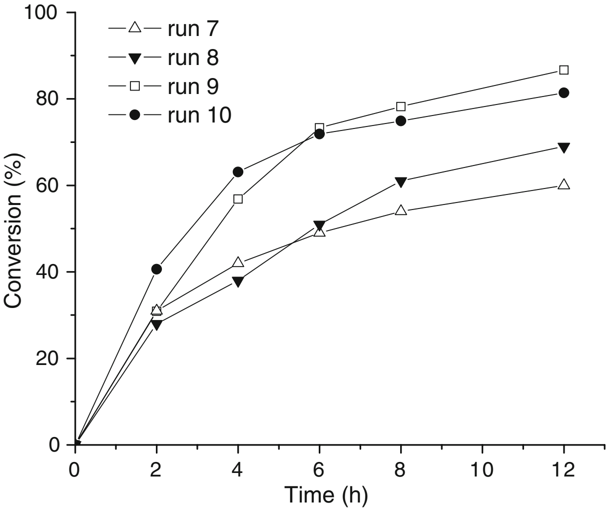
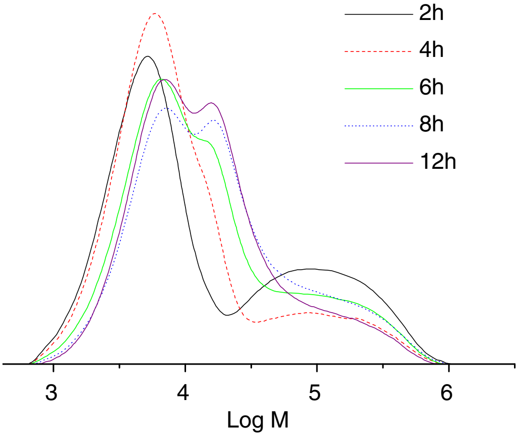


Fig. 5 Plots of conversions versus time for two stage dispersion copolymerization of MMA/TPGDA in the presence of TTC

reported paper [31]. Chain propagation occurs via copolymerization of MMA and MFM before chain transfer takes place to produce a “dormant” polymer which has several pendant acrylate groups coming from MFM units. These pendant acrylate groups, which can be confirmed on the polymer by ^{1}H NMR spectroscopy, participate in polymerization at a later stage to form branched polymers through which propagating chains grow. If the branched polymers still have a number of pendant acrylate groups, they are also “dormant”. The formation of “dormant” branched structures followed by propagating chains growing through pendant acrylate groups repeat several times through polymerization. Finally, a distribution of branched polymer architectures is produced.

According to two stage dispersion polymerization, only MMA polymerized at the nucleation stage while TTC and TPGDA participated after nucleation. Therefore, the polymerization was divided into two stages. The first stage is homopolymerization of MMA in which stable and monodisperse PMMA particles were produced. The second stage is copolymerization of MMA and TPGDA under TTC control. Because TTC has a certain oil/water solubility, it is located on the surface of the particles. MMA and TPGDA were partly distributed inside the particles to swell them and partly dissolved in the medium. Oligo-radicals formed by chain propagation of MMA and TPGDA in the continue phase precipitate from the medium and are captured by the existing particles. As these particles were swollen by MMA, TPGDA and TTC, those oligo-radicals would continue to propagate and transfer inside particles. Since the whole polymerization included homopolymerization and copolymerization, the products contained PMMA and poly (MMA-co-TPGDA) two components. As the conversion at the end of the homopolymerization was about 5%, the composition ratio of PMMA/poly (MMA-co-TPGDA) in the final products was 5/75 (assumed the conversion is 80%).

Fig. 6 GPC traces of the methacrylate copolymer (run 8) synthesised via RAFT dispersion polymerization



The GPC molar mass distribution curves are shown in Fig. 6. The broad peak in the region 10^4–10^6 g/mol is most likely associated with the linear PMMA synthesised in the first stage. This peak did not shift but gradually declined at high conversion. The anterior peak which is probably associated with the branched poly (MMA-co-TPGDA) synthesised in the second stage broadens and develops a shoulder at high molar mass. It had a low molecular weight and narrow distribution due to the control of RAFT agent. At low conversion, most pendant acrylate group of poly (MMA-co-TPGDA) did not react, and the structure of poly (MMA-co-TPGDA) was linear or a small amount of branching. The molecular weight of poly (MMA-co-TPGDA) slowly shifted toward higher value with time, demonstrating the retention of chain-end functionality during the polymerization. Indeed, the data obtained from GPC, using a differential refractive index as detector, are usually lower than the real molecular weight, as branched polymers of a given molecular weight have a smaller hydrodynamic volume than linear polymeric chains of similar molecular weight. In addition, a shoulder peak arose on the high molecular side broadening the distribution, indicating pendant acrylate group gradually took part in the polymerization and poly (MMA-co-TPGDA) turned into branched structure.

The structure of methacrylate copolymer was confirmed by ^{1}H NMR spectra. As shown in Fig. 7a and b, the broad peak centered at 5 ppm were assigned to methine proton and methylene proton next to O=C–O on the TPGDA units, demonstrating the copolymerized of TPGDA on the polymer chain. However, the composition fraction of TPGDA units in the final copolymer calculated by comparing integral area (in Fig. 7a) was 2.13% mole (compared to MMA), less than 4.4% mole in the monomer. This could be related to copolymerization reactivity ratio and conversion. For the copolymerization of MMA (M_1) and TPGDA (M_2), the reactivity ratios are $r_1 = 2.0$ and $r_2 = 0.5$, respectively [32]. Since the rate of consumption of TPGDA (M_2) is slower than MMA (M_1), the composition fraction of TPGDA in the final copolymer lower than that in the initial monomer. Peaks at 6.42, 6.14, and 5.86 ppm were the typical 1H NMR peaks for the acrylate double bond, which resulted from pendant acrylate group. The peaks in Fig. 7a were quite strong, confirming there

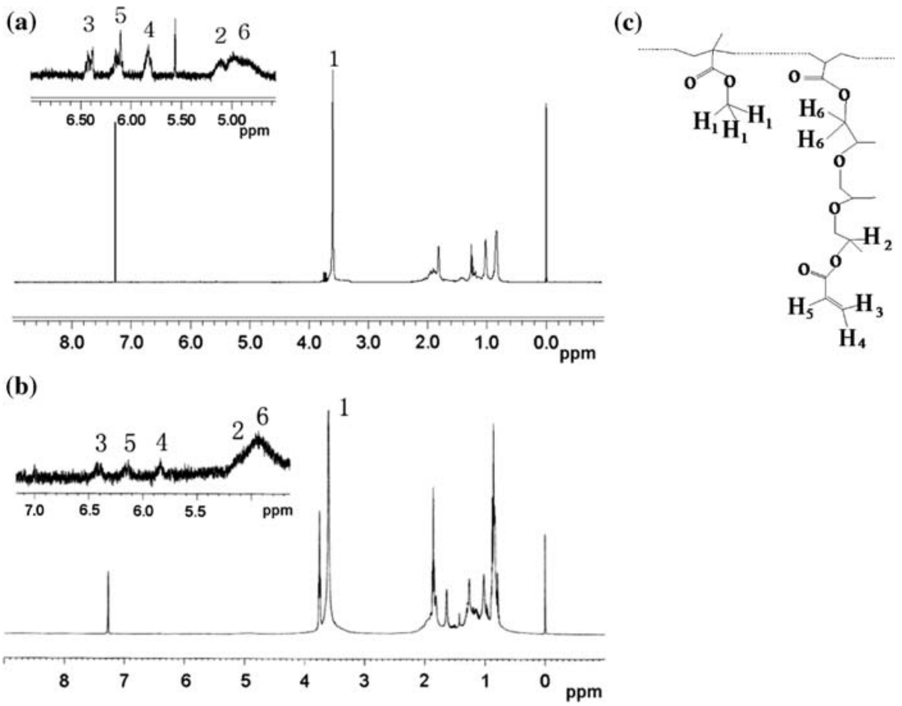


Fig. 7 ^{1}H NMR spectrum of poly (MMA-co-TPGDA): (**a**) run 8, reaction for 12 h, conversion 69%. (**b**) run 10, reaction for 12 h, conversion 82%

were a lot of residual pendant group (70%, calculated by comparing integral area) in the copolymer due to low conversion of polymerization (69%). As increasing PVP concentration increased the conversion, peaks of residual pendant group in Fig. 7 almost disappeared. That is to say at the later stages of the polymerization, the pendent double bonds increasingly react to form higher branched structures.

According to Mark–Houwink equation:

$$[\eta] = KM^{\alpha} \quad (4)$$

Here, $[\eta]$ is intrinsic viscosity of the polymer; K is a constant; α is an exponent related to the molecular shape called Mark–houwink constant. For linear polymer, the Mark–houwink constant α is typically in the region of 0.7. The branched polymer has a smaller value of α from 0.21 to 0.44 because the increase of molecular size with molecular weight is not as rapid in branched polymers as in linear polymers. Assuming the molecular weight obtained from GPC was the real value of the copolymer, we calculated α of the copolymer with the K value (0.078) in the reference [32]. The results of molecular weight, MWD and Mark–Houwink constant α of poly (MMA-co-TPGDA) are listed in Table 2. After the reaction took place for reaction for 2 h, poly (MMA-co-TPGDA) had a low molecular weight, a low MWD and a high Mark–Houwink constant, indicating copolymer was linear or a small amount of branching. As the conversion increase, α gradually reduced from

Table 2 Changes of molecular weight, moleculare weight distribution (MWD) and Mark–Houwink constant α of poly (MMA-co-TPGDA) with polymerization time

Reaction time (h)	Run 9			Run 10		
	Mn (g/mol)	MWD	α^a	Mn (g/mol)	MWD	α^a
2	5,480	1.63	0.582	6,185	2.17	0.594
4	6,554	1.48	0.531	8,748	2.12	0.547
6	7,383	1.66	0.525	8,442	2.26	0.491
8	8,212	1.65	–	8,874	2.20	0.431
12	8,231	1.81	0.517	9,118	2.25	0.406

[a] α was calculated according to [η] measured in toluene at 25 °C, Mn derived from GPC and K=0.078 [32]

0.6 to 0.4 (run 10), demonstrating the transition of copolymer structure from linearity to branching. By comparing run 9 and 10 in Table 2, copolymer of run 9 had typical properties of linear polymer such as narrower MWD and higher α value due to low concentration of TPGDA, indicating the degree of branching of copolymer was low. When the level of MFM increased, α value decreased and MWD broadened, resulting in a more highly branched architecture. In addition to obtaining branched polymers, controlling the extent of branching and preventing gel formation at the same time was a challenge. Thus the extent of branching could be varied by modifying the feed ratio of TPGDA/MMA.

Conclusions

Dispersion polymerization of MMA was carried out in an ethanol/water mixed solvent in the presence of TTC. As TTC delayed nucleation and destroyed colloidal stability of the latex, increasing amount of stabilizer and improving addition of chain transfer agent made it possible to control the particle size and enhance the colloidal stability. Polymerization rate and conversion both increased with increasing concerntration of TTC and PVP.

Branched methacrylate copolymer microspheres were synthesised by copolymerization of MMA and TPGDA in the presence of TTC via two stage dispersion polymerization. The morphology of the microspheres was studied by optical microscope, and the results showed Dn increased with time while keeping a narrow particle size distribution. Dn also increased at a higher mole ratio of TPGDA/MMA and lower concentration of PVP. The copolymer microspheres was confirmed to have two components by GPC: linear homopolymer of MMA and branched copolymer of MMA and TPGDA.

The comonomer TPGDA was further proved to copolymerize into the polymer chain by 1H NMR. But, the composition fraction of TPGDA in the copolymer was lower than that in the initial monomer. This can be explained as TPGDA has a low reactivity ratio toward MMA and the conversion of monomer is low. At later stage of the polymerization, pendant acrylate group is increasingly reactive to form more highly branched structures. The Mark–Houwink constant α of copolymer reducing with conversion from 0.594 to 0.406 also confirmed the branched structure of copolymer. At same time, increasing the concentration of MFM led to higher branched degree of copolymer.

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