Controlled Chain Branching Free Radical Polymerization Manipulate with Trithiocarbonates

Xiao Long Wang, Zhi Chen, Rong Ran

College of Polymer Science and Engineering, State Key Lab for Polymer Materials Engineering, Sichuan University, Chengdu 610065, People's Republic of China

ABSTRACT: Soluble, branched (methyl) methacrylate copolymers have been prepared via facile, one-step, batch solution free radical polymerizations taken to high conversion. Methyl methacrylate (MMA) or methacrylate has been copolymerized with the branching comonomer (BCM) using a trithiocarbonate (TTC) to inhibit gelation. The BCMs employed were tripropylene glycol diacrylate (TPGDA) and trihydroxymethylpropyl triacrylate (TMPTA). Soluble branched copolymers containing unreacted double bonds have been produced and characterized by ^{1}H-NMR spectroscopy. These two brancher monomers have been shown to produce regularly branched material with the small molar mass distributions in the presence of TTC. The results of DSC and Mark–Houwink constant α analyses support the production of the branched architectures. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 2486–2492, 2009

Key words: controlled copolymerization; branched polymer; polymethacrylate; trithiocarbonate

INTRODUCTION

Branched polymers with different architectures have received tremendous attention in recent decades, not only because of their rich morphological textures,[1,2] but also because of their potential applications, such as compatibilizer in polymer blends,[3] as surface modifiers for uses as coatings, adhesives, dispersants, and etc.[4,5] Most hyperbranched polymers are synthesized by step-growth polymerization via polycondensation of AB_x monomers. Here, A and B are the two functionalities that can react with each other but not with themselves. Facile routes to produce hyperbranched polymers via addition polymerization are very rare.[6] Frechet et al.[7] first reported the self-condensing vinyl polymerization (SCVP) process, where a vinyl monomer presents a second functional group that is capable of initiating the polymerization of other vinyl groups. This strategy has been employed in the case of cationic,[7] group transfer,[8] ATRP,[9] RAFT,[10] and nitroxide-mediated[11] vinyl polymerization. However, this process is difficult to exploit industrially, as it requires expensive, tailored vinyl monomers with specific functional groups that require complex syntheses and the polymerizations need to be stopped at low conversions.

Sherrington and his coworkers[12–15] have reported a facile, generic and cost effective route to branched vinyl polymers via conventional free radical polymerization using a multi-functional vinyl comonomer as the branching species, with gelation inhibited by use of a thiol chain transfer agent or indeed a catalytic chain transfer species. The free radical copolymerizations of methyl methacrylate (MMA) and several branching comonomers (BCMs) such as ethylene glycol dimethacrylates with varying lengths of PEG chains, divinylbenzene (DVB), tripropylene glycol (TPGDA), and ethylene glycol diacrylate (EGDA) have been investigated. Soluble branched polymers were obtained in good yield. They have also developed both branched gel-type poly (styrene-*co*-DVB)s and branched macroporous poly(styrene-*co*-DVB)s with a facile one-pot suspension polymerization.[16] Besides using the conventional chain-transfer agent in the synthesis of branched polymers, Sherrington's group, in collaboration with Armes' group, applied copper-mediated living radical polymerization (LRP) and group transfer polymerization to the synthesis of soluble branched polymers in facile one-pot reactions.[17]

Reversible addition fragmentation chain transfer (RAFT) technique is a well-known strategy for the controlled/LRP and has been extensively investigated because of its numerous monomers available under various conditions. RAFT process involves, as the key step, reversible addition-fragmentation chain transfer. The most effective RAFT agents are certain thiocarbonylthio compounds, which commonly are
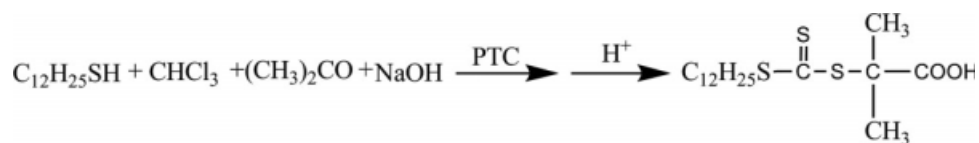
Scheme 1 Synthesize of *S*-1-dodecyl-*S*'-(α, α'-dimethyl-α''-aceticacid) trithioncarbonate.

dithioester and trithiocarbonate (TTC).[18–20] With appropriate choice of the RAFT agent and reaction conditions, RAFT polymerization can be successfully used to produce narrow polydispersity (co)polymers with controlled molecular weights and architectures. Currently, the TTC has attracted much attention because of its ease of synthesis and purification, especially useful for the controlled polymerization of styrene, acrylate, acrylamide monomers, and their derivatives under extremely facile condition. There are some reported literature where the use of RAFT to generate crosslinked gel[21] or hyperbranched polymers.[22–24] Furthermore, RAFT polymerizations have been investigated for the synthesis of hyperbranched PMMA in a one-pot reaction.[25] RAFT appears to be the technique of choice for the production of hyperbranched polymers, via a living polymerization technique, in an industrially viable process.

In our previous research,[26] we studied the free radical polymerization of styrene and butyl acrylate in the presence of TTC, and found that polymerization demonstrated controlled/living characteristics. In this article, we investigate the use of the TTC to produce branched polymer in a one-step, batch solution free radical polymerizations. Soluble, branched (methyl) methacrylate copolymers have been prepared at different conversion by using a RAFT agent (TTC) to inhibit gelation. The structure of polymers was studied via ¹H-NMR. The molecular weight and molar mass distributions of polymers were obtained via conventional GPC. In addition, the Mark–Houwink constant α of polymers at 30°C was also estimated. Typically α of branched polymer varies between 0.5 and 0.3. Finally, the T_g of the branched copolymers was determined by thermal analyses DSC.

## EXPERIMENTAL SECTION

Materials

MMA and Methyl acrylate (MA) (Shanghai Chemical Co., AR) were passed through a column of activated basic alumina (50–200 μm) to remove the inhibitor. Tetrahydrofuran (THF) and carbon disulfide were analytical grade and used after purification. Sodium hydroxide, chloroform, acetone, toluene, dibenzoyl peroxide (BPO), 1-dodecanethiol, hydroquinone, TPGDA, and trihydroxymethylpropyl triacrylate (TMPTA) (Shanghai Chemical Co., AR) were used as received.

Synthesis of *S*-1-Dodecyl-*S*'-(α, α'-dimethyl-α''-aceticacid) trithioncarbonate

The structure of TTC was shown in Scheme 1 and was prepared according to reference.[20] After recrystallization in ethanol, the yellow product was gained (65% yield). (mp: 61–63°C). ¹H-NMR (δ): 0.9 (t, 3H, —CH₃), 1.25–1.50 (m, 20, —CH₂—), 1.65 (s, 6H, —CH₃), 3.29 (t, 2H, —CH₂—S—), 13.05 (s, S, 1H, —COOH) (Fig. 1).

Synthesis of branched polymers in the presence of TTC

Polymers were synthesized via batch solution polymerization in an oil bath thermostatically controlled at 75°C. The synthesis reaction was shown on Scheme 2. A 250 mL three-necked round bottom flask was fitted with a condenser and a nitrogen supply. MMA (20 g, 200 mmol) and TPGDA (4.28 g, 14 mmol) were dissolved in toluene (45 g) using TTC (1.09 g, 3 mmol) as RAFT agent. The polymerization was initiated using BPO. The polymerization was performed up to predetermined time with a continuous flow of nitrogen bubbling slowly through the solution. Aliquots were taken from the reaction mixture at various times, corresponding to different conversions of monomer to polymer. Solutions were cooled immediately and free-radical inhibitor (Hydroquinone) was added. The copolymers were precipitated into *n*-hexane and dried in a vacuum oven overnight at 40°C. Conversions were determined gravimetrically.
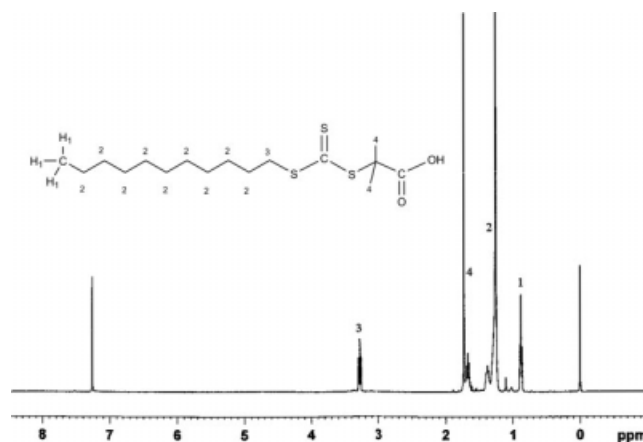
Figure 1 The ¹H-NMR of *S*-1-Dodecyl-*S*'-(α, α'-dimethyl-α''-aceticacid) trithioncarbonate.
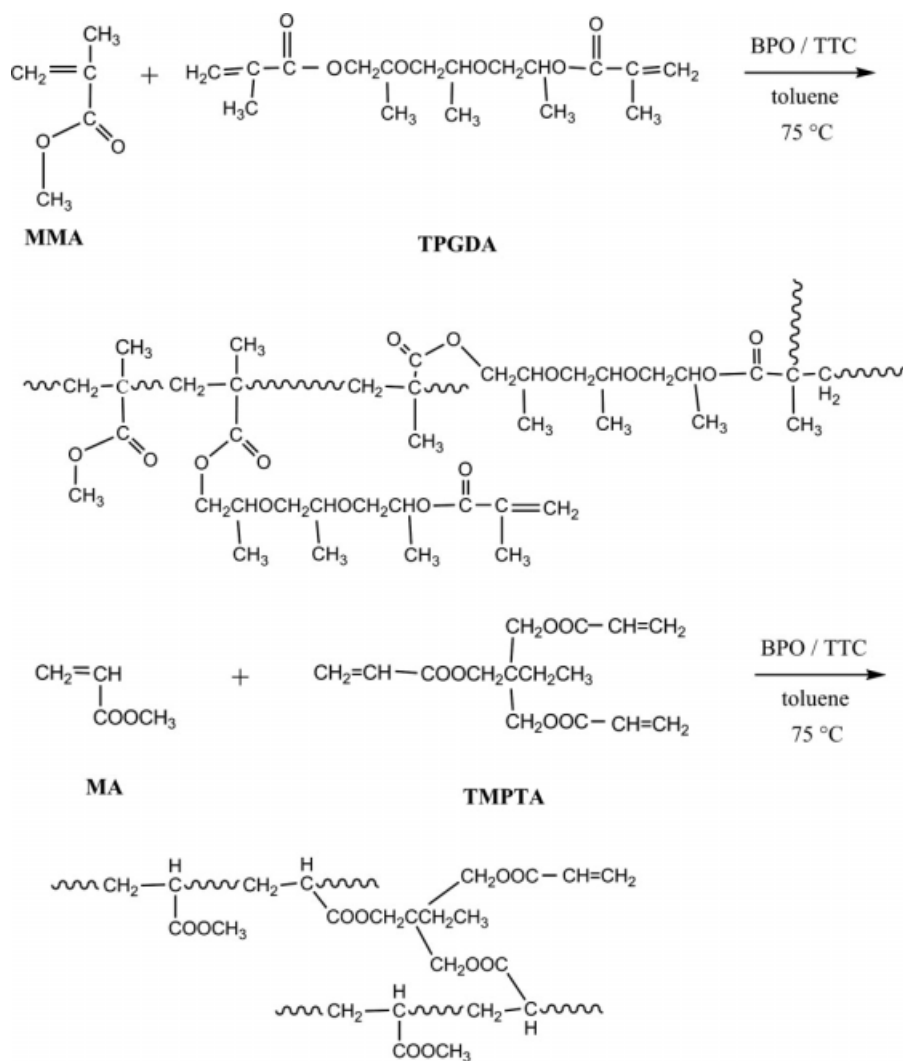
Scheme 2 Synthesize of branched polymers.

Characterizations of polymers

The molecular weight M_n and the molecular weight distribution (MWD) were measured on a Agilent 1100 gel permeation chromatography (GPC) equipped with Pl gel column, mono-disperse PSt as standard, with THF (1.0 mL/min) as eluent. ^{1}H-NMR spectra were analyzed on a Varian Unity Inova 400 instrument with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Melting point of TTCs were measured on X4 melting point microscope instrument. The glass transition temperatures (T_gs) of the prepared branched polymers were determined using a Dupont Company DSC TA2910. The heating rate was set at $10°C/min$ from -10 to $450°C$. Nitrogen was used as an inert gas. The viscosity measurements of copolymer in toluene were performed with Ubbelohde viscometer at $30°C$. Solubility tests were performed by simple visual observation in test tubes placed in an ultrasonic bath for 10 min at room temperature. The solvents tested were THF, chloroform, dimethylformamide, and acetone.

RESULTS AND DISCUSSION

Synthesis of branched polymers via RAFT polymerization

The branched PMMAs were prepared as described in the Experimental Section, following the work of Sherrington and coworkers.[14] We studied the effect of the RAFT agent (TTC) for developing branched polymers, and compare the effect of TTC to that of a traditional chain-transfer agents and catalytic chain-transfer (from Sherrington's initial study). We used a ratio of TPGDA/TTC (14 : 3), which much higher than previously published work. The results obtained are shown in Table I. In the RAFT polymerization manipulate with TTC, gelation occurs at a molar ratio of TPGDA/TTC that is near to five. Soluble products were prepared by batch

TABLE I
Branched Copolymers of MMA Prepared Using TTC

| Entry	Feed ratio (mol) M/BCM/I	Feed ratio (mol) BCM/TTC	Yield (%)	Solubility (0.5 g/mL)	M_n	M_w	M_w/M_n
MMA/TPGDA1	200/14/3.3	15/3	41	No			
MMA/TPGDA2	200/14/3.3	14/3	52	Soluble in all solvents	5323	10235	1.92
MMA/TPGDA3	200/14/2	14/5	43	Soluble in all solvents	5228	9567	1.83
MMA/TPGDA4	200/9.7/2	9.7/10	35	Soluble in all solvents	5497	9320	1.70
MA/TMPTA1	200/4/4	4/1	33	Soluble in all solvents	8370	21800	2.41
MA/TMPTA2	200/4/4	4/2	31	Soluble in all solvents	7630	21400	2.50

T = 80°C; Solvent: toluene (45 mL); Time: 7 h; Solvents tested: THF, CHCl$_3$, DMF, and acetone.
M, monomer; BCM, branching comonomer; I, initiator.

solution polymerization taken to 60% conversion. Sherrington's and Armes' study showed that when the ratio of EGDMA (ethylene glycol dimethacrylate)/DDT (dodecanethiol) is higher than 1.5, gelation occurs in the polymerization system.[16] Compare with mercaptan, TTC has the advantage that much lower quantities are required for effective inhibition gelation in polymerization. Furthermore, copolymerizations of MA and TMPTA (a ratio of TMPTA/TTC = 4.0 : 1.0) were also performed using TTC to inhibit gelation instead of mercaptan (see Table I). However, in both polymerizations of (methyl) methacrylate monomers, TTC can also be used to regulate molecular weight.[20]

Structure characterization of the resulting polymeric products

The ^{1}H-NMR spectra (Figs. 2 and 3) of these soluble polymers confirm their branched structure. A PMMA prepared using MMA/TPGDA/BPO = 100/7/1 and isolated after 5 h showed in Figure 2. Peaks at 6.42, 6.14, and 5.56 ppm were the typical ^{1}H-NMR peaks for the acrylate double bond, which resulted from pendant acrylate group. The signals at 3.5–3.9 ppm correspond to O—CH$_3$ of copolymerized MMA methacrylate ester. The broad peak centered at 5 ppm were assigned to methine proton and methylene proton next to O—C—O on the TPGDA units. The composition of the copolymer and conversion of the pendant acrylate group were calculated by
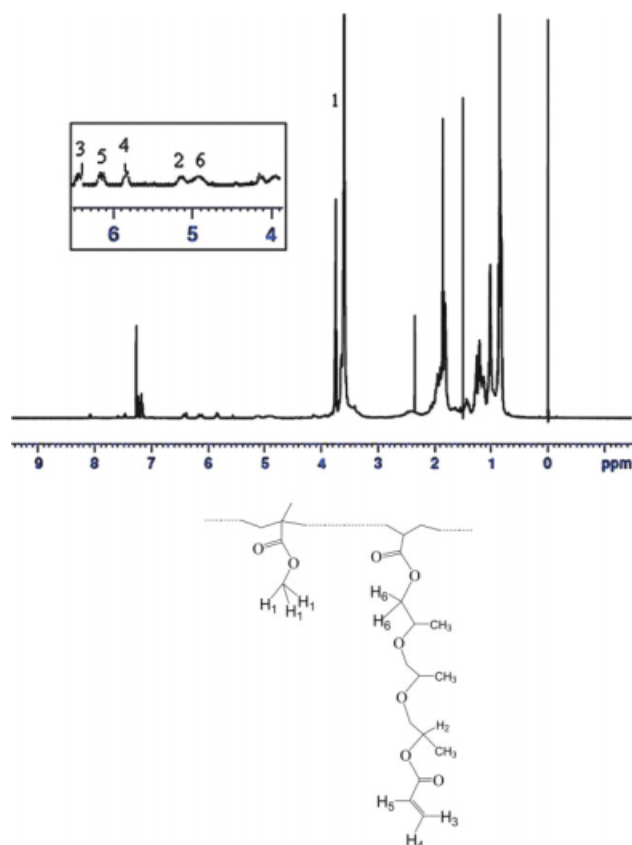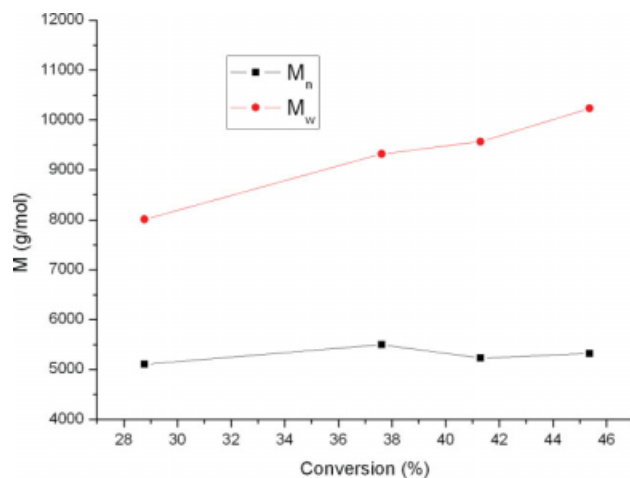

Figure 2 The ^{1}H-NMR of copolymer of MMA and TPGDA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
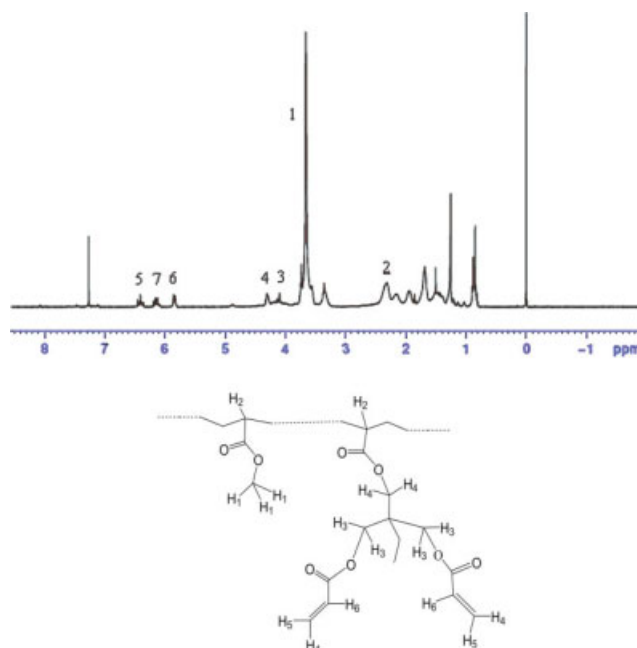
Figure 3 The ^{1}H-NMR of copolymer of MA and TMPTA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 4 The variation of molecular weight averages for poly(MMA-*co*-TPGDA) isolated at various conversions. The molecular weights were obtained from conventional GPC calibrated with linear PSt standards. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
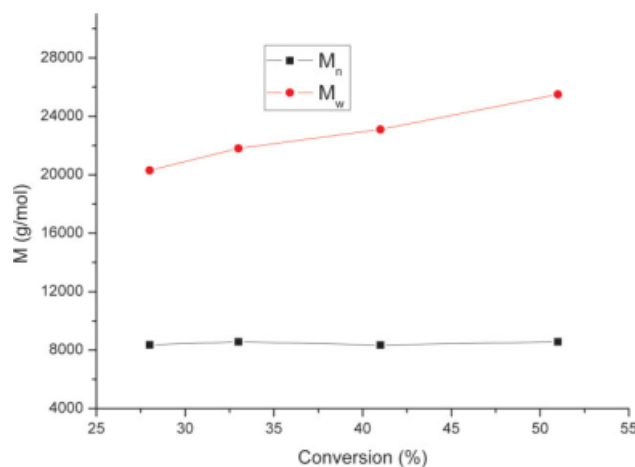

Figure 5 The variation of molecular weight averages for poly(MA-*co*-TMPTA) isolated at various conversions. The molecular weights were obtained from conventional GPC calibrated with linear PSt standards. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

comparing integral area. The result showed that the composition fraction of TPGDA units in the final copolymer was 4.13% mole (compared with MMA), less than 7% mole in the monomer, and the residual pendant group was 75.3%. This could be related to copolymerization reactivity ratio and conversion. For the copolymerization of MMA (M_1) with TPGDA (M_2), the corresponding reactivity ratios were $r_1 \approx 2.0$ and $r_2 \approx 0.5$. It means that TPGDA was not easy to copolymerized onto the polymer chain. The composition fraction of TPGDA in the copolymer was lower than that in the monomer from the beginning of copolymerization.

The ^{1}H-NMR spectrum of branched PMA is shown in Figure 3. The signals at 3.5–3.9 ppm and 2.4 ppm correspond to O—CH$_3$ and —CH (COOCH$_3$)— of copolymerized acrylate methylester (MA), respectively. Characteristic of the branching —CH$_2$OOC— group in the TMPTA residues (4.1 ppm), along with resonances characteristic of the —CH$_2$OOC— group in pendent unreacted TMPTA residues (4.3 ppm) were observed in Figure 3. Peaks at 6.42, 6.14, and 5.8 ppm were the typical ^{1}H-NMR peaks for the acrylate double bond, which resulted from pendant acrylate group. The composition of the copolymer and conversion of the pendant acrylate group were calculated by comparing integral area. The result showed that the composition fraction of TPGDA units in the final copolymer was 1.23% mole (compared with MMA), less than 2% mole in the monomer, and the residual pendant group was 85.1%. In addition, the incorporation of TTC residues into the both branched polymers is also confirmed by the ^{1}H-NMR spectra, and in particular by the presence of the two broad resonances

at 1.3 ppm (corresponding to — (CH$_2$)$_9$—) and at 2.4 ppm (corresponding to —CH$_2$—S—).

The molecular weight of the branched copolymer

The various molecular weight averages obtained from polymers isolated at different conversions via conventional GPC are illustrated in Figure 4 and Figure 5. These results showed that M_n remains fairly constant throughout the polymerization where M_w increase with conversion. Since M_w/M_n, the MWD broadens with conversion and contains an ever increasing high molecular weight tail. This is quite unlike the situation in the conventional free-radical homopolymerzation of MMA to form linear polymer.[15] The molecular weights that were determined in our study are not as high as those expected for a
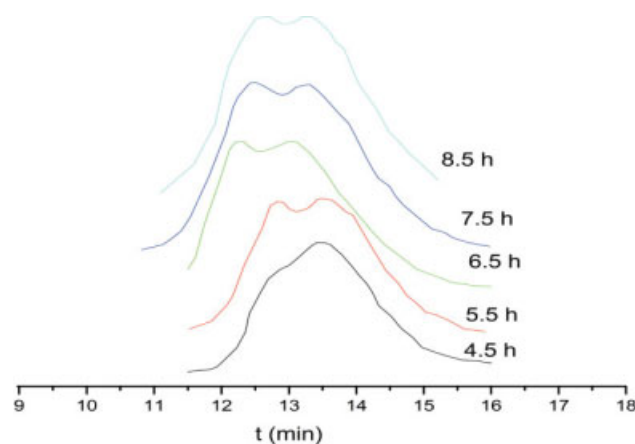
Figure 6 GPC of hyperbranched polymer of MMA and TPGDA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
The T_g and Mark–Houwink Constant α of the Branched Copolymer

Entry	Feed ratio (mol) M/BCM/I	Feed ratio (mol) BCM/TTC	Conversion (%)	T_g (°C)	α[a]
MMA/TPGDA2	200/14/3.3	14/3	60	98	0.383
MA/TMPTA1	200/4/4	4/1	33	7	0.423

$T = 30°C$.
[a] Solvent: toluene.

classic living polymerization system. 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 is possessed by a linear polymeric chain of similar molecular weight.

Figure 6 shows the chromatograms from the GPC for copolymers isolated at different monomer conversions. There are two peaks for every GPC trace of the sample. Different peaks indicate components of different branching generations, and the anterior peak may correspond to the component formed by combination of two branched prepolymers through TTC or biradical coupling.[27] At low conversion, most pendant acrylate group of poly (MMA-co-TPGDA) didn't react, and the structure of poly (MMA-co-TPGDA) was linear or little branched. 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. In addition, a anterior peak arose on the high molecular side broaden the distribution, indicating pendant acrylate group gradually took part in the polymerization and poly (MMA-co-TPGDA) turned into branched structure. This behavior is in agreement with the observations made from the ^{1}H-NMR analyze, that is to say that at the later stages of the reaction the pendent double bonds increasingly react to form more highly branched materials.

The T_g and Mark–Houwink constant α of the branched copolymer

The branching information is extracted using equations that have been developed from basic geometry and fundamental polymer solution theory. The most basic information is derived from the relationship between intrinsic viscosity and molecular weight.

$$[\eta] = KM^\alpha$$

This is often referred to as the Mark–Houwink relationship. The exponent α has characteristic values and is typically in the region of 0.7 for linear homopolymers in a good solvent with a random coil conformation. The increase of molecular size with molecular weight is not as rapid in branched polymers as in linear polymers. This has the effect of lowering the slope of the Mark–Houwink plot giving smaller values of α. The average Mark–Houwink constant α for the branched PMMA was 0.383, branched PMA was 0.423 (Table II). This data compare well with data for branched polymers where average α value tend to vary from 0.5 to 0.2 depending on the degree of branching. To our knowledge, there is little information published on the chemical or physical architecture composition distribution of branched polymers.

Branched polymers usually have lower T_g values than their linear counterparts. Some reports on the T_g of highly branched polymers indicated that the T_g values are greatly affected by terminal functional groups,[15,23] with decreases in T_g following increases in the concentration of chain end groups. On the other hand, the restriction in mobility that is caused by the branching points should increase T_g. DSC analyses were performed on the branched poly-(MMA-co-TPGDA) and poly-(MA-co-TMPTA) (Table II). As expected, the poly-(MMA-co-TPGDA) show lower $T_g = 98°C$ than it of linear PMMA ($T_g = 105°C$). Simultaneously, the poly-(MA-co-TMPTA) show higher $T_g = 4°C$ than it of linear PMA ($T_g = 6°C$). This suggests that the branched copolymer produced with the larger number of end groups likely to increase free-volume. This data correlates well to the situation with branched condensation polymers where T_gs tend to be much lower than linear analogues with the nature of the high end group concentration having a strong influence.[28–30] Again, these analyses confirm the branched structure of the copolymer.

CONCLUSIONS

The TTC was applied for the first time to prepare branched polymer with TPGDA or TMPTA as the branching agent. The soluble, branched polymers were obtained at different conversion. The chain architecture was investigated by ^{1}H-NMR analyses. The molecular weight and molar mass distributions of polymers were obtained via conventional GPC. The results show that the branched polymer

obtained via RAFT-agent-mediated polymerization presented a relative narrow polydispersity and lower molecular weight. Furthermore, the Mark–Houwink constant α of the branched poly- (MMA-*co*-TPGDA) and poly (MA-*co*-TMPTA) at 30°C were much smaller than 0.5, resulting from high degree of branching. Finally, the T_g of branched copolymers were determined by thermal analyses DSC. The lower T_g shows that the PMMA produced with the larger number of end groups.

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