

A Di-*Tert*-Butyl Acrylate Monomer for Controlled Radical Photopolymerization

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ABSTRACT: A new di-*tert*-butyl acrylate (diTBA) monomer for controlled radical polymerization is reported. This monomer complements the classical use of *tert*-butyl acrylate (TBA) for synthesis of poly(acrylic acid) by increasing the density of carboxylic acids per repeat unit, while also increasing the flexibility of the carboxylic acid side-chains. The monomer is well behaved under Cu(II)-mediated photoinduced controlled radical polymerization and delivers polymers with excellent chain-end fidelity at high monomer conversions. Importantly, this new

diTBA monomer readily copolymerizes with TBA to further the potential for applications in areas such as dispersing agents and adsorbents. © 2016 Wiley Periodicals, Inc. *J. Polym. Sci., Part A: Polym. Chem.* **2017**, *55*, 801–807

KEYWORDS: atom transfer radical polymerization (ATRP); controlled radical photopolymerization; diacid; dispersants; living polymerization; photopolymerization; poly(acrylic acid); synthesis

INTRODUCTION Poly(acrylic acid) (PAA) and polyacrylate salts serve many diverse roles in modern society, including applications such as adsorbents,^{1,2} scale inhibitors,³ dispersants,⁴ and thickeners.^{5,6} These applications are driven by a polymer backbone decorated with carboxylic acids that allows for multivalent interactions with a variety of particles, surfaces, or small molecules through hydrogen bonding and/or ionic interactions [Fig. 1(A)]. While PAA has demonstrated great commercial success in these areas, several other acid containing polymers and their copolymers (e.g., maleic acid (co)polymers^{7–9} and itaconic acid (co)polymers^{10,11}) have also demonstrated impressive materials properties. Given the ability to use controlled radical polymerization techniques, such as ATRP,^{12,13} SET-LRP,¹⁴ RAFT,¹⁵ and NMP^{16–18} to control the polymerization of acrylates and to a lesser extent maleic acid, the opportunity exists to further refine and tailor properties through the controlled introduction of novel building blocks.¹⁹

To address this challenge, we have developed a novel monomer, di-*tert*-butyl acrylate [diTBA, Fig. 1(B)], from low-cost, renewable starting materials.

Z.A.P. and R.B.Z. contributed equally to this work

Additional Supporting Information may be found in the online version of this article.

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EXPERIMENTAL

Materials

All materials were purchased from Sigma Aldrich and used as received unless otherwise stated; α -ketoglutaric acid ($\geq 99\%$), sulfuric acid (ACS reagent 95–98%), sodium borohydride (powder, 98%), acryloyl chloride (97% purity), ethyl bromoisobutyrate (EBiB) (98% purity), copper (II) bromide (CuBr₂) (99% purity), tris[2-(dimethylamino)ethyl]amine (Me₆-Tren) (97%), *tert*-butyl acrylate (TBA) (98%), trifluoroacetic acid (TFA) (99%), and (trimethylsilyl)diazomethane TMSCHN₂ (2.0 M solution in diethyl ether). Triethylamine TEA (99%), and all solvents were purchased from Fisher Scientific and used as received. *Tert*-butyl acetate (99.8%) was purchased from Chem Impex Int'l Inc. and used as received. TBA monomer was passed through a column of basic alumina (~150 mesh, Brockmann I grade) prior to use to remove the inhibitor.

Instrumentation

The source of UV light used for all polymerizations was a commercial UV nail gel curing lamp (available from a range

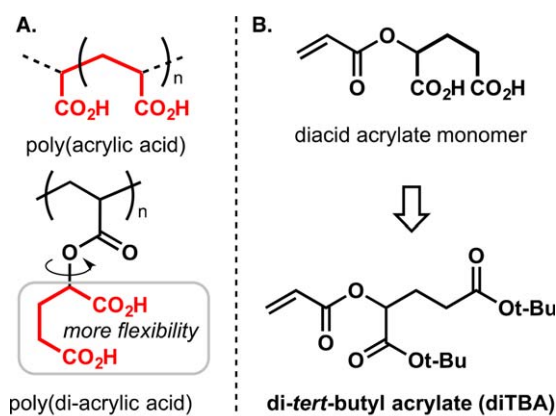


FIGURE 1 (A) Structures of poly(acrylic acid) and branched poly(di-acrylic acid) target polymers. (B) Structures of the di-acid and di-*tert*-butyl acrylate monomers. [Color figure can be viewed at wileyonlinelibrary.com]

of suppliers) ($\lambda_{\max} \sim 360$ nm) equipped with four 9W bulbs. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian 400 MHz, 500 MHz or 600 MHz spectrometer. Size exclusion chromatography (SEC) for molecular weight analysis, relative to linear polystyrene standards, was performed on a Waters 2690 separation module equipped with Waters 2414 refractive index and 2996 photodiode array detectors using CHCl_3 containing 0.25% triethylamine as eluent at a flow rate of 1 mL/min. Mass spectrometry was performed on a Waters GCT Premier time-of-flight mass spectrometer (EI and FD). Matrix-Assisted Laser Desorption Ionization time of flight (MALDI-ToF) spectrometry was conducted using a Bruker Microflex LRF MALDI TOF mass spectrometer, equipped with a 60 Hz nitrogen laser at 337 nm. Solutions in tetrahydrofuran of dithranol as a matrix (saturated solution, 10 μL), sodium trifluoroacetate as cationization agent (1.0 mg/mL, 2 μL) and sample (1.0 mg/mL, 10 μL) were mixed, and 0.7 μL of the mixture was applied to the target plate. Spectra were recorded in linear mode. Thermal gravimetric analysis (TGA) was performed using a TA Discovery TGA 1-0055 V5.7 at a heating rate of 10 $^\circ\text{C}/\text{min}$ using 1–10 mg of sample in an alumina sample cup atop a platinum or ceramic hanging pan (under nitrogen). The data was analyzed on Trios software V3.3. Differential Scanning Calorimetry (DSC) was performed using a TA Instruments DSC Q2000-0998 V9.9 at a heating/cooling rate of 10 $^\circ\text{C}/\text{min}$ using 3–5 mg of sample in a sealed aluminum pan, with respect to an empty aluminum reference pan. Three cycles of heating and subsequent cooling were performed. The data was analyzed on Universal Analysis 2000 4.4A software.

Synthesis of Di-*Tert*-Butyl Acrylate (*diTBA*) Monomer Di-*Tert*-Butyl 2-Oxopentanedioate (**1**)

H_2SO_4 (7.3 mL, 137 mmol) was added to a stirred suspension of α -ketoglutaric acid (20 g, 137 mmol) in *t*-BuOAc (700 mL). The reaction mixture was stirred at rt overnight, then washed with ethyl acetate, 2N NaOH solution (2×100 mL), brine (150 mL), and dried over MgSO_4 . The crude product was concentrated and purified by column chromatography on silica

gel (75:25 Hex:Et₂O) to afford the product as pale yellow oil (19 g, 53%).

¹H NMR (600 MHz, in CDCl_3 , δ in ppm) 3.04 (t, $J = 6.6$ Hz, 2H), 2.55 (t, $J = 6.6$ Hz, 2H), 1.54 (s, 9H), 1.43 (s, 9H); ¹³C NMR (600 MHz, in CDCl_3 , δ in ppm) 193.94, 171.41, 160.16, 84.15, 81.07, 34.36, 28.96, 28.18, 27.94.

Di-*Tert*-Butyl 2-Hydroxypentanedioate (**2**)

NaBH_4 (4.5 g, 118 mmol) was added portion wise to a stirred solution of di-*tert*-butyl 2-oxopentanedioate (20 g, 79 mmol) in MeOH (400 mL) at 0 $^\circ\text{C}$. After 30 min, water was added to the reaction mixture and MeOH was evaporated. The product was extracted with DCM (2×50 mL), the organic layers were combined, washed with brine, and dried over MgSO_4 . The crude product was passed through a short silica gel column (75:25 Hex:Et₂O) to afford the product as colorless oil (20 g, 97%).

¹H NMR (600 MHz, in CDCl_3 , δ in ppm) 4.07 (dd, $J = 8.0, 4.1$ Hz, 1H), 2.40 (ddd, $J = 15.9, 9.1, 6.7$ Hz, 1H), 2.32 (ddd, $J = 16.3, 9.2, 5.7$ Hz, 1H), 2.11 – 2.05 (m, 1H), 1.86 – 1.79 (m, 1H), 1.49 (s, 9H), 1.44 (s, 9H); ¹³C NMR (600 MHz, in CDCl_3 , δ in ppm) 174.16, 172.67, 82.68, 80.50, 69.84, 31.07, 29.76, 28.19, 28.11.

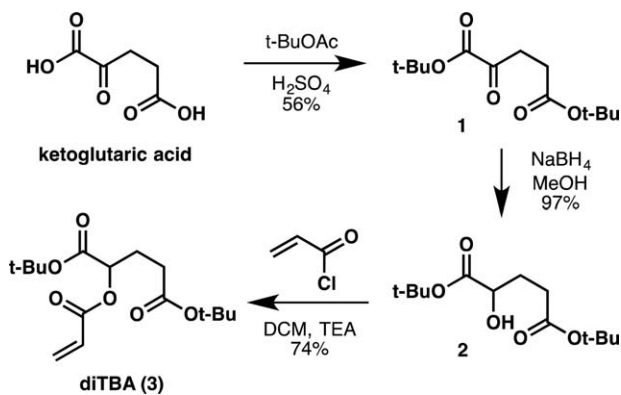
Di-*Tert*-Butyl 2-(Acryloyloxy)Pentanedioate (**3**, *diTBA*)

Di-*tert*-butyl 2-hydroxypentanedioate (15 g, 58 mmol), and Et₃N (16 mL, 115 mmol) were dissolved in dry DCM (300 mL) and cooled to –78 $^\circ\text{C}$. Acryloyl chloride (9.4 mL, 115 mmol) was added drop wise to the reaction vessel. The reaction mixture was stirred at 0 $^\circ\text{C}$ for 15 min, then quenched with water, diluted with 1N HCl. The organic layer was washed with brine, dried over MgSO_4 , concentrated under reduced pressure and purified by column chromatography on silica gel (75:25 Hex:Et₂O) to afford the product as colorless oil (14 g, 77%).

¹H NMR (600 MHz, in CDCl_3 , δ in ppm) 6.45 (dd, $J = 17.4, 1.3$ Hz, 1H), 6.16 (dd, $J = 17.4, 10.5$ Hz, 1H), 5.87 (dd, $J = 10.5, 1.3$ Hz, 1H), 4.95 (dd, $J = 8.3, 4.6$ Hz, 1H), 2.42 – 2.27 (m, 2H), 2.20 – 2.27 (m, 1H), 2.12 – 2.05 (m, 1H), 1.44 (s, 9H), 1.43 (s, 9H); ¹³C NMR (600 MHz, in CDCl_3 , δ in ppm) 171.74, 168.79, 165.48, 131.81, 127.81, 82.45, 80.79, 71.97, 31.20, 28.19, 28.06, 26.57.

General Polymerization Conditions for the Preparation of *diTBA* (Co)Polymers

$\text{Cu}^{\text{II}}\text{Br}_2$ (0.02 equivalents relative to monomer) DMF (3.2 M for *diTBA* homopolymerizations, 4 M for 1:3 TBA:*diTBA*, 4.5 M for 1:1 TBA:*diTBA*, and 6 M for both 3:1 TBA:*diTBA* and TBA homopolymerizations), Me₆-Tren (0.12 equivalents relative to initiator), acrylate monomer(s) and initiator were added sequentially to a vial equipped with a magnetic stir bar and septum screw cap. The mixture was sparged with nitrogen for 10 min then placed under a UV-light (365 nm), stirring for 12 h. The reaction mixture was run through a plug of basic alumina with Et₂O, and then the organic fraction was washed with H₂O (3×50 mL), dried with MgSO_4 (anhydrous) filtered



SCHEME 1 Synthesis of di-*tert*-butyl acrylate (diTBA) from ketoglutaric acid.

and concentrated under reduced pressure. For DP50 and lower molecular weight targets the polymers were purified with silica-gel column chromatography, wet packed with 80:20 (Hex:Et₂O), then eluted with 80:20 (Hex:Et₂O) (KMnO₄ stain to visualize monomer) followed by 25:75 (Hex:Et₂O) to remove the polymer (bromocresol blue stain to visualize the polymer fractions). Concentration of the polymer fractions under reduced pressure gave foamy white solids. For DP100 and larger targets the polymers were precipitated into 1:1 MeOH:H₂O, decanted and washed with 1:1 MeOH:H₂O 3 × 100 mL, then dissolved in Et₂O, dried with MgSO₄ (anhydrous), filtered and concentrated to obtain white foamy solids. Isolated yields ranged from 65% to 92%.

General Conditions for the Deprotection of diTBA (Co)Polymers

The diTBA (co)polymer (1 g) was dissolved in neat TFA (10 mL) and stirred overnight at rt. TFA was removed under reduced pressure. The crude material was dissolved in THF and precipitated from hexanes to give diAA (co)polymers as white solids with quantitative yields (> 99%).

General Conditions for the Methylation of diAA (Co)Polymers

Excess (trimethylsilyl)diazomethane (TMSCHN₂) was added to a solution of the diAA (co)polymer (until yellow color persists) in MeOH at 0 °C. The reaction mixture was stirred for an additional 10 min at this temperature then left overnight at rt. It was quenched with HOAc, and concentrated under reduced pressure to afford the diMA polymers as white solids in good yields (90–95%).

RESULTS AND DISCUSSION

DiTBA Monomer Design and Synthesis

The di-*tert*-butyl acrylate monomer (diTBA, Fig. 1) was designed with a number of considerations in mind. First, the relative arrangement of carboxylate groups in the monomer structure mimics the 1,3 spacing of carboxylates in the PAA backbone [highlighted by red bonds, Fig. 1(A)]. The incorporation of two carboxylic acids into each repeat unit also increases the charge density with regard to polymer chain

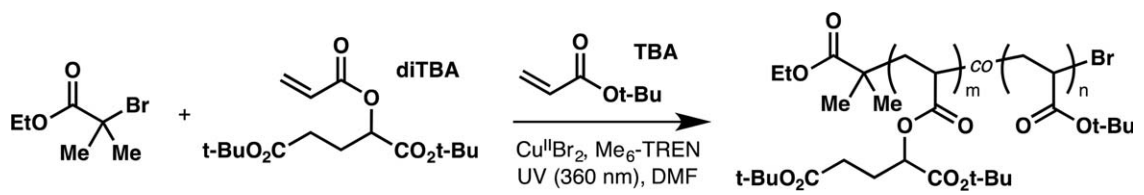
length, similar to itaconic acid/maleic acid monomers. In comparison to these derivatives, the acids should possess enhanced flexibility and rotational freedom since they are no longer directly attached to the polymer backbone. It is anticipated that the combination of higher carboxylate density and branched architecture will aid in the binding of polymers to particles, such as calcite or titania.²⁰ Finally, to ensure compatibility with a range of polymerization techniques and simplify handling, protected carboxylic acids were employed as *tert*-butyl esters.

To investigate these hypotheses, a short and efficient synthesis of the desired diTBA monomer was developed starting from α -ketoglutaric acid, an inexpensive and commercially available compound (Scheme 1).²¹ First, the two carboxylic acids were converted to *tert*-butyl esters using an acid-mediated transesterification with *tert*-butyl acetate. Next, keto-ester **1** was cleanly and selectively reduced to α -hydroxy ketone **2** with sodium borohydride. Subsequent acylation without purification with acryloyl chloride yielded the desired diTBA monomer (**3**) as a colorless oil in three steps and 41% overall yield. Notably, this process is operationally straightforward, efficient, and scalable.

DiTBA Polymerization and Characterization

To polymerize the new diTBA monomer, our attention was directed to recent advances in photo-induced controlled radical polymerization.^{22–39} A recent report by Haddleton and coworkers demonstrated that *tert*-butyl acrylate could be polymerized to very high conversions while retaining excellent end group fidelity (>99%) using catalytic Cu^{II}Br₂ and an aliphatic amine ligand, Me₆-Tren, in the presence of UV ($\lambda_{\text{max}} \approx 360\text{nm}$) light.²⁵ The reported conditions proved to also be effective for the polymerization of diTBA when dimethylformamide (DMF) was used as a solvent in combination with ethyl α -bromoisobutyrate as an initiator. Following this protocol, well-defined diTBA polymers were prepared with degrees of polymerization (DP) ranging from 10 to 400 (Table 1, Entries 1–6). Each of the polymerizations proceeded to high conversions (>94% - 12 h reaction time) and displayed low dispersities ($\bar{D} < 1.25$) by size exclusion chromatography (SEC) analysis in chloroform relative to poly(styrene) standards. The polymers were fully characterized by ¹H NMR with changes in several diagnostic protons allowing for structural analysis. Figure 2 shows the diTBA monomer (top) and the corresponding homopolymer (bottom). After polymerization, all of the olefinic protons (*a*–*c*) in the diTBA monomer were incorporated into the backbone of the new polymer. Characterization is particularly enabled by a diagnostic proton, *a*, present on each of the polymer side chains at 4.7 ppm. When coupled with the isolated chain-end protons, *b*, at 4.1 ppm and the *tert*-butyl protons, *c*, the degrees of polymerization could be readily determined and in excellent agreement with the theoretical values.

The high end-group fidelity of this polymerization was further established by MALDI-ToF-MS analysis and interrogation of the reaction kinetics. The mass spectrum of poly(diTBA)₁₀ is shown in Figure 3(A). Periodic peaks separated by 314

TABLE 1 Cu^{II}-Photomediated Radical Polymerization of diTBA and TBA Monomers


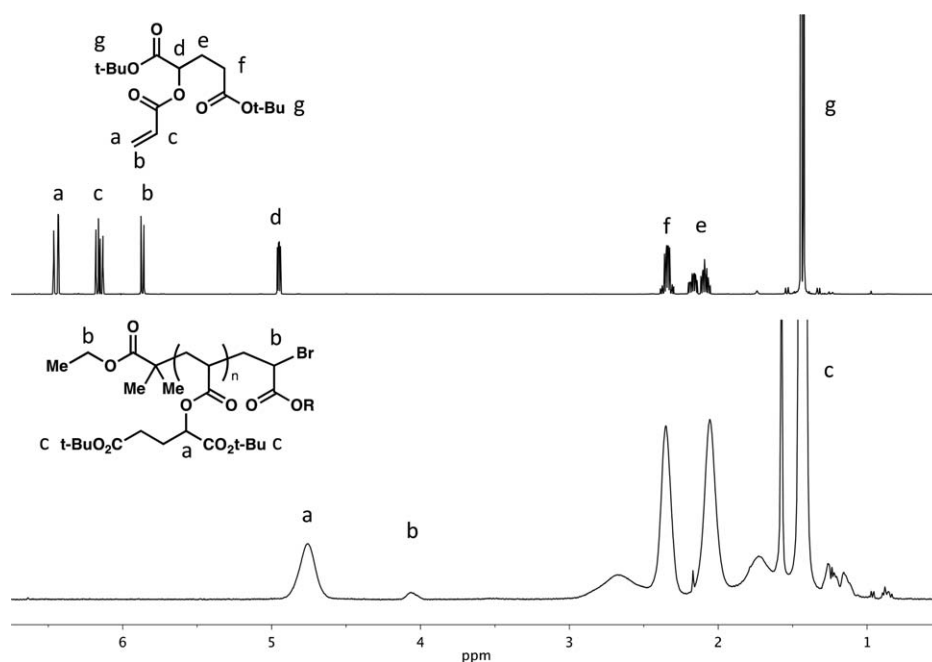
Entry	DiTBA(m):TBA(n)	M:l	Conversion (%) ^a	DP ^a	M _n (kDa) ^b	<i>D</i>	T _{d5%} (°C) ^c	T _g (°C)
1	1:0	10	96	10	2.3	1.09	200	14
2	1:0	25	94	27	4.2	1.10	201	24
3	1:0	50	94	51	7.5	1.13	204	29
4	1:0	100	97	99	13.2	1.15	204	30
5	1:0	200	96	195	17.3	1.24	205	30
6	1:0	400	96	383	22.5	1.20	204	31
7	3:1	50	93	51	7.1	1.15	200	26
8	1:1	50	91	50	6.6	1.14	195	25
9	1:3	50	92	49	6.6	1.12	189	27
10	0:1	50	99	52	5.8	1.09	186	35

^a Determined with ¹H-NMR.^b Chloroform SEC relative to polystyrene standards.^c Temperature at 5% mass loss.

mass units correspond to the molecular mass of each diTBA monomer and each major peak correlates to the predicted value for a [poly(diTBA)_n][•]Na⁺ species containing ethyl isobutyrate and bromide chain-ends [Fig. 3(B)]. Minor peaks separated by 57 mass units represent losses of isobutylene from the *tert*-butyl esters during ionization. Finally, a kinetic study of the polymerization targeting DP 50 displayed the expected linear relationship of ln([M]₀/[M]_t) versus time

further supporting the controlled living radical nature of the photoinduced method utilized (Fig. 4).

With the establishment of a convenient and effective method to polymerize the diTBA monomer, the potential of copolymerization with *tert*-butyl acrylate was explored. Under similar reaction conditions, copolymers with diTBA:TBA monomer feed ratios of 3:1, 1:1, and 1:3 were prepared. The monomer

**FIGURE 2** ¹H NMR spectra in CDCl₃ of the diTBA monomer (top) and poly(diTBA) (bottom).

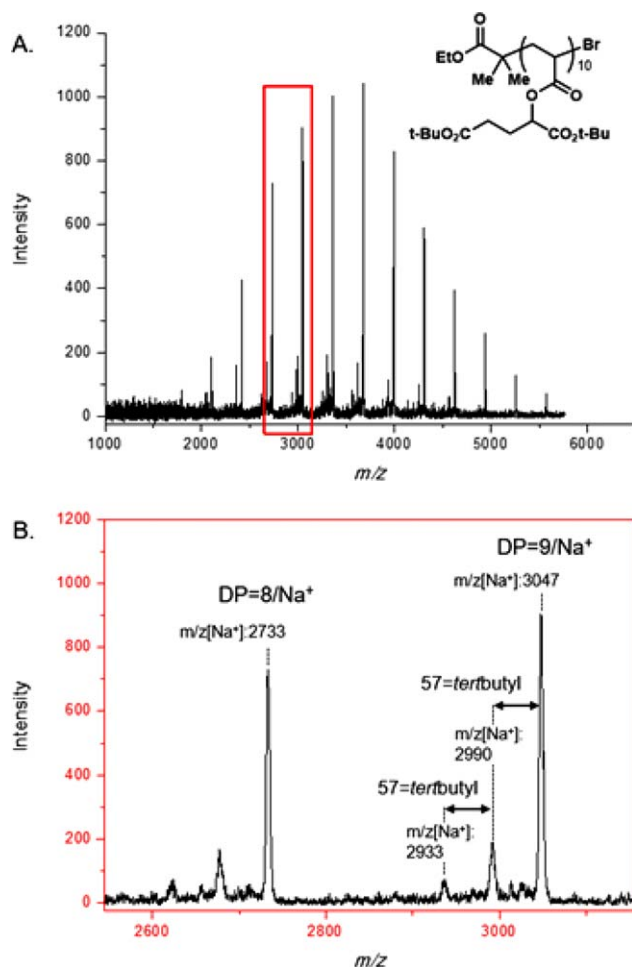


FIGURE 3 MALDI-ToF-MS spectra (A) entire spectrum of poly-(diTBA)₁₀ and (B) expanded view of the boxed section highlighting the periodic spacing of monomer and end-group fidelity. [Color figure can be viewed at wileyonlinelibrary.com]

concentration was increased with the addition of TBA to maintain a similar viscosity to the homopolymerization of diTBA. Notably the diTBA monomer was found to readily copolymerize with TBA at nearly identical rates. Using the diagnostic proton of the diTBA side-chain, (4.7 ppm, Fig. 2) it was found that the feed ratio was equal to the copolymer composition at all conversions permitting straightforward access to desired copolymer compositions without the generation of gradient copolymers.

The thermal properties of diTBA (co)polymers were then evaluated using thermogravimetric analysis (TGA; Fig. 5, Supporting Information Figs. S3.1, and S3.2) and differential scanning calorimetry (DSC; Supporting Information Figs. S3.3 and S3.4). Similar to poly(*tert*-butyl acrylate), the glass transition temperature (T_g) of the diTBA homopolymers were molecular weight dependent. As the size increases from oligomer DP 10 (Entry 1) to DP 50, the T_g increases from 14 °C to 30 °C, where it reaches a plateau (Entries 5 and 6).^{40,41} Interestingly, the T_g of ~ 30 °C is similar to that of poly(*t*-butyl acrylate) (~ 35 °C) with all copolymers displaying

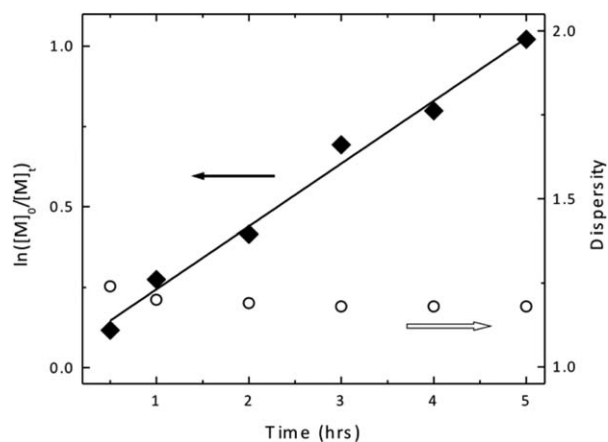


FIGURE 4 Kinetic plot of diTBA₅₀ polymerization demonstrating linear kinetics while maintaining low dispersities.

approximately the same glass transition temperature (Entries 7–9). In analogy with poly(*t*-butyl acrylate), the thermal stability of poly(diTBA) has a well-defined two-step degradation profile (Fig. 5).⁴² As expected, substantial molecular weight loss occurs at ~200 °C corresponding to the conversion of the *tert*-butyl groups to carboxylic acids with concomitant loss of isobutylene. This relative mass loss is consistent with the *tert*-butyl content of the diTBA homopolymer (~36%). Consistently, the relative mass loss of the copolymers at this temperature steadily increased as the *tert*-butyl acrylate ratio increased, since *tert*-butyl acrylate is ~44% wt% isobutylene. On further heating to ~250 °C, a second step is observed in the diTBA containing polymers that correlates with the loss of a glutamic acid molecule. The relative

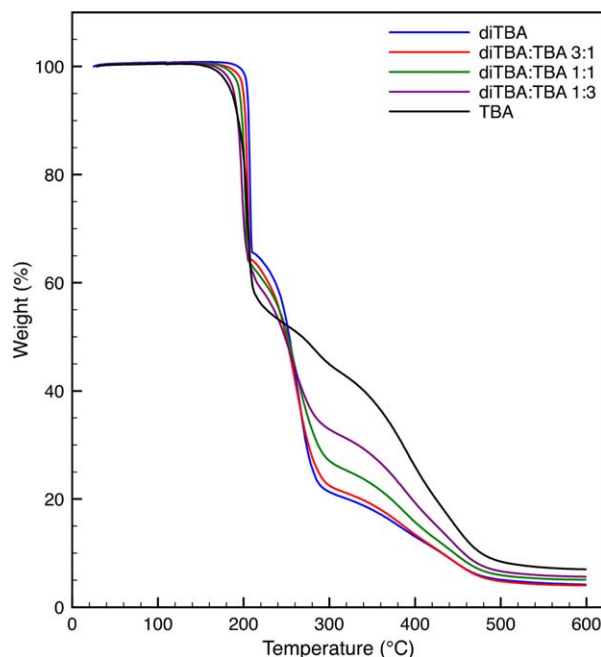
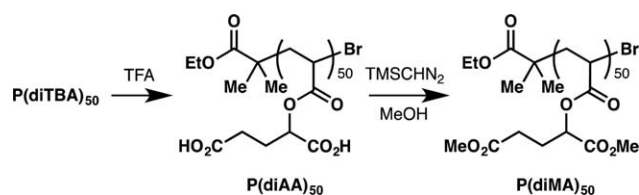


FIGURE 5 TGA thermograms for poly(diTBA)₅₀, poly(diTBA/TBA)₅₀ copolymers, and poly(TBA)₅₀. [Color figure can be viewed at wileyonlinelibrary.com]



SCHEME 2 Deprotection of P(diTBA)₅₀ to P(diAA)₅₀ with TFA, followed by methylation with TMS-diazomethane.

mass loss in each (co)polymer also correlates to the degree of diTBA monomer incorporation, with the diTBA homopolymer losing an additional 41 wt%.

To take advantage of these (co)polymers for targeted applications as anti-scalants or dispersants, the *tert*-butyl groups were converted to the free carboxylic acid form, poly(diacrylic acid) (P(diAA)). This was quantitatively achieved by treatment of the P(diTBA)₅₀ polymer (Scheme 2) with trifluoroacetic acid (TFA) at room temperature. The complete disappearance of the *tert*-butyl proton signals in the ¹H NMR (Supporting Information Fig. S4.1) coupled with infrared absorption spectroscopy supports complete formation of the diacid with minimal anhydride formation (Supporting Information Fig. S4.2). To ensure that no degradation or reaction of the diacid side chains occurred, the P(diAA) polymer was converted to the dimethyl ester, p(diMA), by treatment with TMS-diazomethane for ease of characterization (Scheme 2). After the reaction, quantitative methylation was determined by ¹H NMR integration, again suggesting little-to-no anhydride formation (Supporting Information Fig. S4.3). SEC analysis of poly(diMA)₅₀ shows a slight decrease in molecular weight (consistent with the conversion of the *tert*-butyl ester to methyl esters), but with no change in the dispersity of the polymer (Fig. 6). Further evidence of the polyacid structure was demonstrated through titration experiments (Supporting

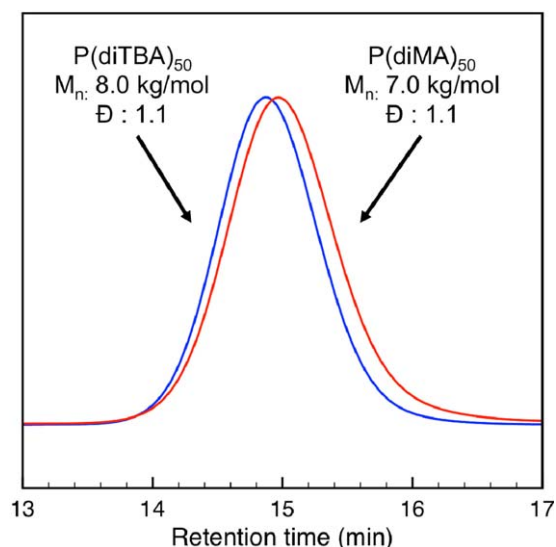


FIGURE 6 SEC traces of p(diTBA)₅₀ and p(diMA)₅₀ in chloroform versus PS standards. [Color figure can be viewed at wileyonlinelibrary.com]

Information Fig. S5). With these experiments, a full range of diacrylic acid polymers is obtainable ranging from homopolymers to copolymers with varying degrees of TBA incorporation. The facile tunability of carboxylic acid density along the backbone of AA-diAA copolymers provides an excellent platform to further evaluate the effect of small-branched structures on the ability to bind surfaces, metals, and small molecules.

CONCLUSIONS

Di-*tert*-butyl acrylate (diTBA), a new functional diacid monomer for controlled radical polymerization, was rationally designed, polymerized, and characterized. Notable features are increased carboxylic acid content per polymer repeat unit relative to traditional TBA-based polymers and greater side chain mobility. Furthermore, the monomer efficiently copolymerizes with *tert*-butyl acrylate thereby permitting further engineering of these branched motifs into existing polyTBA, as well as other acrylate-based monomers. Investigation into the utility of these polymers as dispersants, anti-scalants, and metal chelators is currently underway.

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