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Atom transfer radical polymerization of methyl acrylate from a multifunctional initiator at ambient temperature

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Abstract

A multifunctional initiator for ATRP has been synthesized by reacting a hyperbranched polyether, based on 3-ethyl-3-(hydroxymethyl)oxetane, with 2-bromo-isobutyrylbromide. The macroinitiator contained approximately 25 initiating sites per molecule. It was used for the atom transfer radical polymerization of methyl acrylate mediated by Cu(I)Br and tris(2-(dimethylamino)ethyl)amine (Me_6-TREN) in ethyl acetate at room temperature. This yielded a co-polymer with a dendritic-linear architecture. The large number of growing chains from each macromolecule increases the probability of inter-and intramolecular reactions. In order to control these kinds of polymerizing systems and prevent them from forming a gel, the concentration of propagating radicals must be kept low. The polymerizations under these conditions were well controlled. When a ratio of initiating sites-to-catalyst of 1:0.05 was used, the polymers from all of the reactions had a low polydispersity, ranging from 1.1 to 1.4. None of the polymerizations under these conditions gave gelation. Monomer conversions as high as 65% were reached while maintaining control over the polymerization. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Atom transfer radical polymerization; 'Living'/controlled radical polymerization; Multifunctional initiator

1. Introduction

The interest in macromolecular architecture has increased dramatically in recent years. Dendritic polymers, i.e. dendrimers and hyperbranched polymers, have received considerable attention due to their unique properties and potential applications [1–3]. Dendritic polymers are based on AB_x-monomers and in principle most known polymer-forming reactions can be used for their synthesis, such as condensation reactions [4–6], cationic procedures [4], ring-opening polymerization [7–11] and free-radical procedures including controlled/'living' free radical polymerizations [12,13].

The combination of dendrimer synthesis and controlled radical polymerization is an interesting field that yields new polymeric materials with controlled topology [14].

One of the most widely studied controlled radical polymerization techniques is atom transfer radical polymerization (ATRP). Since it was discovered independently by Matyjaszewski and Wang [15,16] and Sawamoto et al. [17] ATRP has been thoroughly investigated. The ATRP process uses an alkyl halide as initiator, and a metal in its lower oxidation state with complexing ligands [15–22]. The process involves the successive transfer of the halide from the dormant polymer chain to the ligated metal complex, thus establishing a dynamic equilibrium between active and dormant species. ATRP has proven to be a powerful tool in the synthesis of polymers with narrow polydispersities and controlled molecular weight.

ATRP can also be used to accomplish hyperbranched polymers if a monomer with both an initiating and a propagating function is used [23]. A hybrid dendritic-linear architecture is obtained if ATRP is carried out on a hyperbranched or a dendritic core, i.e. a hyperbranched macroinitiator [14,24–32].

The aim of this work was to elaborate an ATRP system for a multifunctional initiator, viable at room temperature. It was also desirable to reach relatively high monomer conversion while maintaining control over the polymerization in order to waste as little as possible of the monomer. The macroinitiator was synthesized from hyperbranched polyethers polymerized from 3-ethyl-3-(hydroxymethyl)oxetane [11], Fig. 1, esterified with 2-bromo-isobutyrylbromide. It was used for the atom transfer radical polymerization of methyl acrylate (MA) in the presence of Cu(I)Br and tris(2-(dimethylamino)ethyl)amine (Me_6-TREN) [33].

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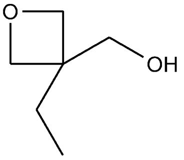


Fig. 1. Structure of 3-ethyl-3-(hydroxymethyl)oxetane.

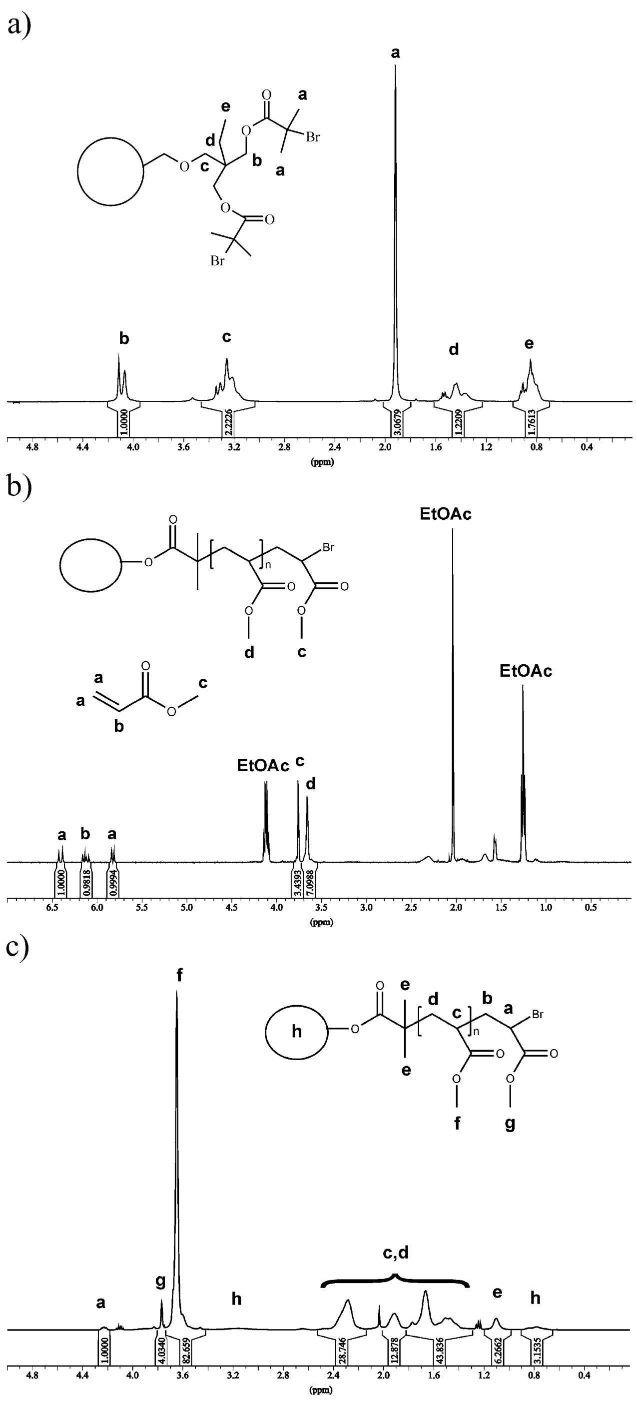


Fig. 2. (a)^{1}H NMR (in $CDCl_3$) and peak assignments of the macroinitiator. (b) ^{1}H NMR (in $CDCl_3$) and peak assignments of the reaction mixture, containing monomer, polymer and EtOAc. (c) ^{1}H NMR (in $CDCl_3$) and peak assignments of the resulting polymer, with traces of EtOAc remaining.

2. Experimental section

2.1. Materials

The hydroxy-functional polyoxetane was prepared as reported in the literature [11] from 3-ethyl-3-(hydroxymethyl)oxetane. Tris(2-(dimethylamino)ethyl)amine (Me_6-TREN) was prepared according to Ciampolini and Nardi [34] from tris(2-aminoethyl)amine (98%, Aldrich). All other chemicals were used as received.

2.2. Characterization

Infrared spectra were recorded on a Perkin–Elmer Spectrum 2000 FTIR equipped with a MKII Golden Gate™, Single Reflection ATR System from Specac Ltd, London, UK. The ATR-crystal was a MKII heated Diamond 45° ATR Top Plate. ^{1}H NMR spectra were recorded on a 400 MHz Bruker Aspect NMR, using $CDCl_3$ as a solvent. Molecular weights and polydispersities were measured with Size Exclusion Chromatography (SEC) on a Waters 717 plus autosampler and a Waters model 510 apparatus equipped with two PLgel 10 μm mixed-B columns, 300×7.5 mm (Polymer Labs, UK), with $CHCl_3$ as the mobile phase, 1 ml min^{-1}. Linear polystyrene standards were used for calibration, ranging from 1 700 to 706 000 g mol^{-1}. Thermal analysis was performed on a Mettler DSC 820 calibrated according to standard procedures. Glass transition temperatures were determined as the inflexion points in the heat-flow curve from the second cooling. The analysis was carried out under nitrogen using a heating and cooling rate of 10 °C min^{-1}.

2.3. Synthesis of Macroinitiator

4.00 g (34.5 mmol hydroxyl-groups) polyoxetane was dissolved in tetrahydrofuran (THF, 50 ml), 0.21 mg (1.7 mmol) *N*,*N*-dimethylaminopyridine and 3.84 g (37.9 mmol) triethylamine were added. The flask was then cooled in a water/ice bath. 7.93 g (34.5 mmol) of 2-bromoisobutyryl bromide was diluted in 10 ml THF and added dropwise to the solution while stirring. The reaction was left to reach completion for approximately 24 h. The solution was precipitated in cold (−78 °C) methanol, the residue was filtered, dried under vacuum yielding a colorless sticky solid. The yield was 25%.

^{1}H NMR (400 MHz, $CDCl_3$): 4.11–4.07 (br, m, $-CH_2$ OOC–), 3.34–3.22 (br, m, $-CH_2CO-$), 1.92 (s, $-C(CH_3)_2$ Br), 1.67–1.36 (br, m, $-CH_3$), 0.93–0.83 (br, m, $-CH_2-$), Fig. 2a.

2.4. General procedure for polymerization from macroinitiator

The synthesis is exemplified by entry 6 in Table 1. 0.50 g of the macroinitiator (1.98 mmol *tert* Br-groups) was placed in a flask and dissolved in 8.5 g of ethyl acetate (EtOAc).

Table 1
Polymerizations with methyl acrylate at room temperature, using Me_6-TREN as a ligand and Cu(I)Br as a catalyst

No.	[M]/[I]/[Cu(I)]/[L]	EtOAc (w/w, %)	Time (min)	M_n[a] (g mol^{-1})	PDI	DP_{SEC}	DP_{NMR}	M_n[b] (g mol^{-1})
1	30:1:0.05:0.05	33	20	32 950	1.25	12	14	36 880
2	50:1:0.05:0.05	33	45	42 100	1.13	16	20	49 800
3	50:1:0.05:0.05	33	40	48 200	1.23	19	28	67 010
4	50:1:0.05:0.05	33	60	50 850	1.22	20	31	73 470
5	100:1:0.1:0.1	33	55	86 700	1.84	37	67	150 950
6	100:1:0.05:0.05	33	150	84 250	1.42	36	70	157 410
7	150:1:0.05:0.05	25	120	95 450	1.28	41	87	194 000

[a] Molecular weight measured by SEC.
[b] Molecular weight calculated from ^{1}H NMR.

17.0 g (198 mmol) MA, 21 mg (0.1 mmol) Me_6-TREN and 14 mg (0.1 mmol) Cu(I)Br were added and the flask was sealed with a rubber septum. The flask was evacuated and back-filled with Ar-gas three times. During this procedure a small amount of EtOAc and MA was evaporated, but since such large amounts of these two compounds were used in every polymerization it was found to be negligible. However, the degassing was performed for the same time period for each polymerization. The polymerization started immediately upon degassing and was left to proceed at room temperature for 2.5 h. For conversion measurements samples were withdrawn with a syringe at time intervals. The withdrawn samples were analyzed with ^{1}H NMR of the crude product in $CDCl_3$, Fig. 2b. At the end of the reaction the viscosity had increased dramatically. The reaction mixture was diluted with THF and passed through a column of aluminum oxide (neutral) in order to remove most of the Cu-complex. The solvents were evaporated and the product was dried under vacuum. A pale green, sticky polymer was produced, colored by traces of copper.

3. Results and discussion

The aim of the study was to develop an ATRP system viable for polymerization at room temperature using a multifunctional initiator. It is desirable to reach high monomer conversions when using multifunctional initiators while maintaining control over molecular weights and polydispersity.

3.1. Synthesis of macroinitiator

The hydroxyl functional hyperbranched polyether was converted into a polyfunctional macroinitiator by converting the end-groups into tertiary bromoester-groups, which are known to be effective initiators for ATRP of acrylates. As can be seen in Fig. 3, the macroinitiator was successfully synthesized with complete conversion of the hydroxyl groups. The polyether shows a broad peak around 3300 cm^{-1}, originating from the OH-end group, which completely disappears after the reaction with 2-bromoisobutyryl bromide. The macroinitiator shows a peak around 1730 cm^{-1} which is not present in the polyether. This peak originates from the carbonyl in the bromoester group.

The yield was low due to the sticky nature of the product, making the work-up procedures difficult.

3.2. Polymerization from the macroinitiator

The macroinitiator was used to polymerize methyl acrylate using the technique of ATRP, Scheme 1. The macroinitiator contained approximately 25 initiating sites per molecule. The large number of growing chains from each macromolecule causes an increased probability of intermolecular reactions. For example, Frey et al. [30] observed gelation after 35% monomer conversion when a multifunctional initiator was used for ATRP in bulk. They attributed the gelation to coupling reactions between propagating radicals. In order to prevent a polymerizing system from forming a gel, the concentration of propagating radicals has to be kept low. This can be accomplished in different ways. Diluted systems, for example, give a lower concentration of radicals. This can be done either by adding a solvent or by stopping the reaction after very low conversion of the monomer, thus allowing the excess monomer to dilute the system. Another approach is to lower the amount of catalyst used, thus creating fewer radicals. In our system polymerization had to be performed in ethyl acetate since

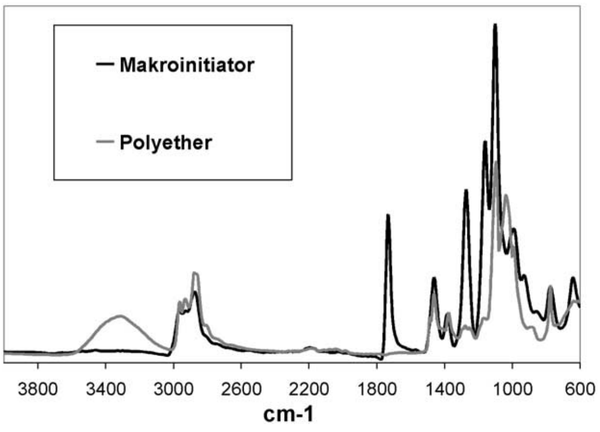
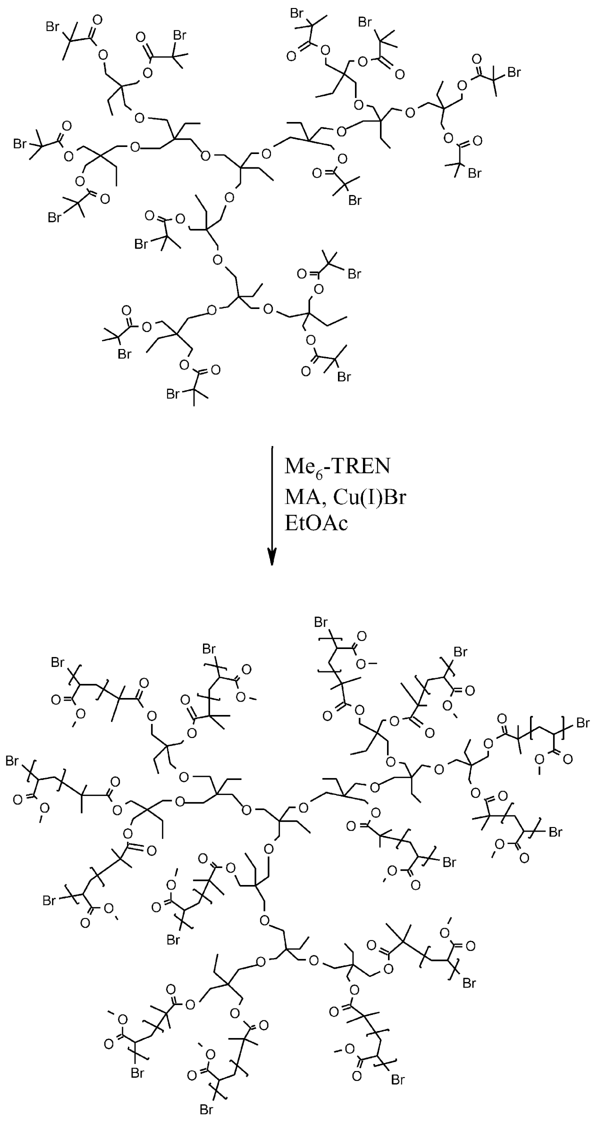


Fig. 3. FT-IR of the polyether and the macroinitiator.



Scheme 1. Polymerization of methyl acrylate from the hyperbranched macroinitiator (simplified drawing).

the attempted bulk polymerizations resulted in polymers with high polydispersity. Furthermore, in these reactions the ratio of initiating sites-to-catalyst ([I]/[Cu(I)]) could not exceed 1:0.1 in order to obtain a controlled polymerization. The most successful polymerizations with respect to conversion and control were performed when using a ratio of 1:0.05.

The chemical nature of the ligand plays an important role in the success of controlled polymerization. Me$_6$-TREN has earlier been shown to be an effective ligand for polymerization of MA at room temperature [33].

As can be seen in Table 1, methyl acrylate was successfully polymerized from the macroinitiator using Me$_6$-TREN as a ligand. The polymerization was fast at room temperature. When stirring was no longer possible due to high viscosity, the reaction was stopped by adding THF and allowing air into the system.

As can be seen in Fig. 2a the ratio of the integral originating from the methyl groups (6H) in the bromoester (denoted **a** in Fig. 2a) and the integral from the methyl groups (3H) originating from the polyether (denoted **e** in Fig. 2a) should be about 2:1. The methyl groups from the bromoesters will shift from about 1.9 ppm in the macroinitiator to about 1.1 ppm in the co-polymer. If all the initiating sites in the macroinitiator initiate polymerization the ratio of the integral from this shifted peak (denoted **e** in Fig. 2c) and the integral from the methyl groups originating from the polyether (denoted **h** in Fig. 2c) should remain the same, about 2:1. As can be seen in Fig. 2c, this is the case. The peak from the macroinitiator is, however, very small and the integral can only roughly be determined, and it is therefore difficult to confirm if all the initiating sites are active.

Molecular weights and polydispersities were determined by size exclusion chromatography, using linear polystyrene standards. The obtained molecular weights are probably much lower than the actual values since highly branched polymers are known to have smaller hydrodynamic volume than their linear analogues [3]. The M_n has therefore also been calculated from ^{1}H NMR. The determined polydispersity values might not agree completely with the real values since hybrid dendritic-linear polymers are analyzed.

When a ratio of initiating sites-to-catalyst of 1:0.05 was used the polymers from all the reactions had a low polydispersity, ranging from 1.1 to 1.4, indicating a well-controlled polymerization. The SEC curves of the polymers were narrow and monomodal, as can be seen in Fig. 4. When the ratio of initiating sites-to-catalyst was raised to 1:0.1 there was a sudden increase in the polydispersity, which shows a lack of control over the polymerization at this concentration of radicals.

In order to obtain different degrees of polymerization (DP), the ratio of monomer-to-initiating sites was varied. The DP was calculated both from SEC and from ^{1}H NMR. When calculating the DP from SEC the assumption was made that the macroinitiator had 25 initiating sites and that each initiating site gave rise to one polymer arm. The number of initiating sites was calculated from SEC analysis

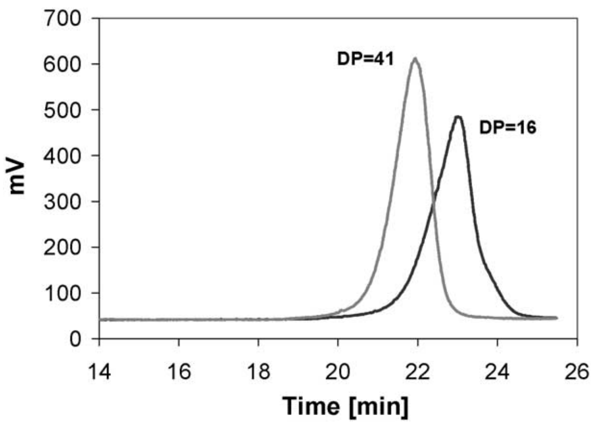


Fig. 4. GPC traces of the resulting polymer (entries 2 and 7 in Table 1).

of the polyether. The number of hydroxyl groups equals the molecular weight of the polyether divided by the mass of the repeating unit (116 g mol^{-1}). This result was in agreement with ^{1}H NMR spectroscopy.

In calculating the DP of the PMA arms in the hybrid dendritic-linear molecule the molecular weight of the macroinitiator was 6750 g mol^{-1}, as measured by SEC. Fig. 2c shows an example of ^{1}H NMR of a resulting polymer, entry 3 in Table 1. Calculation of the DP from ^{1}H NMR was done by adding the integrals from the peaks of all the methyl groups (3H) in the polymer (assigned **g** and **f** in Fig. 2c) and dividing that sum with half of the integral from the peak of the methyl groups (6H) in the macroinitiator (assigned **e** in Fig. 2c). Another way of calculation the DP is to divide the sum of the integral from **f** and **g** in Fig. 2c with the integral from **a** taken three times. In Fig. 2c these two ways both give a DP of 28. A third way is to divide the sum of the integrals from all the methyl groups in the polymer (**f** and **g** in Fig. 2c) with the integral from the terminal methyl groups in the chain (**g** in Fig. 2c). However, the peaks **f** and **g** in Fig. 2c are poorly separated and this calculation should only be considered a rough estimation. As expected, the DPs calculated from SEC are lower than the DPs calculated from ^{1}H NMR. The difference between the two values increases with increasing molecular weight.

Conversion can be calculated from ^{1}H NMR of the crude product. An example of this can be seen in Fig. 2b where conversion is calculated by dividing the integral from the peak from the methyl group in the chain (denoted **d** in Fig. 2b) with the sum of the integral from all the methyl groups in both the monomer and the polymer chain (denoted **c** and **d**). From Fig. 2b it can be calculated that the overall conversion in this case was about 65%.

Kinetic experiments show that the reaction rate rapidly decreases around 70–80% conversion and longer reaction times do not give an increase in conversion, Fig. 5. This is suggested to be due to the persistent radical effect, converting the catalyst irreversibly from Cu(I) to Cu(II). This indicates that side reactions begin to take place at higher conversions, which results in an increase in the polydispersity index. The increase is rather small but this could be attributed to the fact that the initial concentration of Cu(I) is very low and only a few side reactions need to take place to convert all the Cu(I) to Cu(II). This might not give rise to a large change in the polydispersity.

Table 2
Thermal characterization by DSC revealed two T_gs for each copolymer

No.	DP$_{SEC}$	T_g^1 (°C)	T_g^2 (°C)
1	12	≈ -40	3
2	19	≈ -40	6
3	36	≈ -40	12

As can be seen from Fig. 2c, the relationship between peak **a** (originating from the proton on the same carbon as the bromide in each chain end) and peak **e** should be 1:6. This is clearly the case in the spectrum, which shows that there has been essentially no loss of the bromide atom at the chain ends, hence the reaction is 'living'. This is further evidence of the controlled nature of the polymerization and shows that side reactions, such as termination, have been suppressed.

3.3. Thermal analysis

Differential scanning calorimetry on the PMA-grafted polymers exhibited two glass transitions (Table 2, Fig. 6) indicating that the resulting block-copolymers are phase-separated. The lower glass transition (approximately −40 °C) is unaffected by the length of the PMA grafts and therefore assumed to originate from the hyperbranched polyether core. In contrast, the higher glass transition is affected by the length of the grafts and therefore suggested to originate from the poly(methyl acrylate) grafts.

4. Conclusion

A hyperbranched macroinitiator has been synthesized by reacting a hyperbranched polyether, based on 3-ethyl-3-(hydroxymethyl)oxetane, with 2-bromo-isobutyrylbromide. The macroinitiator was used for the atom transfer radical polymerization of methyl acrylate yielding a polymer with a

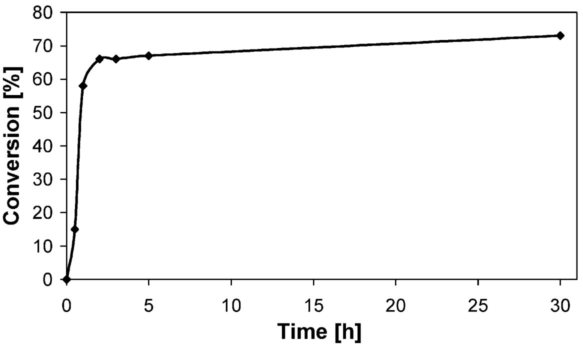


Fig. 5. Kinetic plot for the polymerization of MA from the macroinitiator. Conversion was calculated from ^{1}H NMR of the crude product.

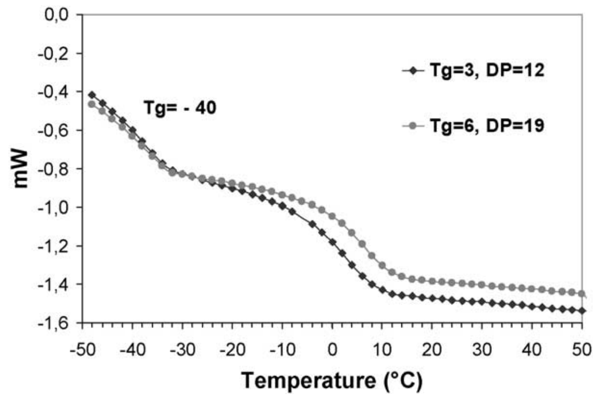


Fig. 6. DSC traces of the resulting polymer (entries 1 and 3 in Table 1).

dendritic-linear architecture. The resulting polymers had low polydispersity, down to 1.1. The polymerizations proceeded at room temperature in a controlled manner when Cu(I)Br was used as catalyst and Me$_6$-TREN as ligand. The most successful polymerizations were performed when using a ratio of initiating sites-to-catalyst of 1:0.05. None of the polymerizations under these conditions gave gels. Conversions as high as 65% were reached while maintaining control over the polymerization.

Acknowledgements

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