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Block, blocky gradient and random copolymers of 2-ethylhexyl acrylate and acrylic acid by atom transfer radical polymerization

Kris R.M. Vidts, Bart Dervaux, Filip E. Du Prez*

Ghent University, Department of Organic Chemistry, Polymer Chemistry Research Group, Krijgslaan 281 (S4-bis), 9000 Ghent, Belgium

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Abstract

The controlled synthesis of low-T_g poly(2-ethylhexyl acrylate) (P2EHA) and derived random, block and blocky gradient copolymers via atom transfer radical polymerization (ATRP) is described. After optimizing the reaction conditions for the homopolymerization of 2EHA via ATRP, the synthesis of a variety of copolymers with poly(*t*-butyl acrylate) (P*t*BuA) was investigated. First, AB-block copolymers were targeted, starting from P2EHA and P*t*BuA as macroinitiators. Second, random copolymers of *t*BuA and 2EHA with different monomer ratios were synthesized. Finally, the synthesis of ''blocky'' gradient copolymers via a one-pot procedure was investigated, starting with the homopolymerization of *t*BuA, followed by the addition of 2EHA. The hydrolysis of the P*t*BuA-segments to poly(acrylic acid) (PAA), which was carried out with methanesulfonic acid, resulted in block, blocky gradient and random copolymers consisting of PAA and P2EHA. Solubility testing of the copolymers in slightly basic water (pH ~ 9) demonstrated that the gradient structure significantly enhances solubility compared to the block copolymer structures with equal composition. The polymers have been characterized by MALDI-TOF MS, GPC and ^{1}H NMR.

Keywords: Poly(2-ethylhexyl acrylate); Block copolymers; Atom transfer radical polymerization

1. Introduction

Poly(2-ethylhexyl acrylate) (P2EHA) is used in several applications, including pressure-sensitive adhesives, because of its low T_g-value of −50 °C, good oil resistance and adhesion to various substrates. Moreover, it is polar compared to elastomers based on hydrocarbons. Conventionally, P2EHA and similar low-T_g products are made by emulsion polymerization in an uncontrolled manner [1]. Since recently, several groups report on the (mini)emulsion polymerization by controlled radical polymerization techniques of low-T_g polymers such as poly(2-ethylhexyl methacrylate) (P2EHMA, $T_g = -10$ °C) [2–4]. An advantage of having controlled molecular weight and narrow polydispersity polymers, particularly for low-molecular weight products, is the low concentration of volatile organic compounds (VOC). For polymers made by free, uncontrolled radical polymerization, higher fractions of small, volatile products are usually observed [2]. Moreover, the controlled radical polymerization techniques also allow for preparing more complex segmented structures that are applied in a broad field of applications including compatibilizers, dispersants, adhesives and for drug delivery. For many examples, amphiphilic structures with controllable solubility are desired, often obtained by the introduction of a pH-responsive polymer segment, such as poly(acrylic acid) (PAA), in combination with a hydrophobic polymer segment.

The aim of this work was to make a wide set of copolymers of 2-ethylhexyl acrylate (2EHA) and acrylic acid (AA) in a controlled way by atom transfer radical polymerization (ATRP), for their possible use in fields where the incorporation of very low-T_g 2EHA-segments in copolymer structures is of particular interest. This controlled radical polymerization technique allows to control the molecular weight and to obtain a low polydispersity index and high end group functionality. The latter is important for the design of more complex polymer structures. ATRP is commonly not able to polymerize

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* Corresponding author. Tel.: +32 92644503; fax: +32 92644972.
E-mail address: filip.duprez@ugent.be (F.E. Du Prez).

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acidic monomers such as AA due to a side reaction of the monomer with the metal complex and quaternization of the nitrogen-containing ligands [5,6]. Therefore, PAA is generally obtained from precursor monomers such as *t*-butyl acrylate (*t*BuA), benzyl acrylate or 1-ethoxyethyl acrylate, followed by hydrolysis [7], debenzylation [8] or thermolysis [6,9], respectively. In this work, the polymerization of *t*BuA, followed by hydrolysis, was the selected method because the ATRP of this monomer [10–14] and the hydrolysis conditions [7] have already been extensively described in literature. Polymerization of 2EHA on the other hand has not been investigated in detail yet by ATRP [15]. To our knowledge, clear evidence of a controlled radical polymerization of this monomer has not been presented until now. In most cases, polymers with relatively high polydispersity indexes and molecular weights have been obtained, also in patent literature [16].

Therefore, the starting point of this research was to revisit the synthesis of P2EHA via ATRP. Then, the AB-block copolymerization with P*t*BuA as second segment and precursor of poly(acrylic acid) (PAA) has been studied. Also the controlled synthesis of blocky gradient and random copolymers consisting of *t*BuA and 2EHA was of particular interest for comparison reasons. Advances in molecular design of macromolecules with well-defined structures make it possible to investigate the effects of variations in the structure of macromolecules on their properties. This will be illustrated by the comparison of the solubility behaviour in water of the different types of PAA/P2EHA copolymers after hydrolysis. A more detailed study on the phase behaviour of the copolymers by light scattering and other advanced methods is in progress, but outside the scope of this paper.

2. Experimental part

2.1. Materials

*t*BuA (Fluka, 98+%) was purified by vacuum distillation (30 °C/2 mm Hg). 2EHA (Acros, 99+%; 98–99 °C/18 mm Hg) and N,N,N',N'',N''-pentamethyldiethylene-triamine (PMDETA, Aldrich, 99%; 83–84 °C/18 mm Hg) were also distilled before use. CuBr (Aldrich, 99%) and CuCl (Aldrich, 99.999%) were purified by washing with acetic acid, filtering with ethanol and drying under vacuum [17]. Me_6–TREN was synthesized out of tris(2-aminoethyl)amine (TREN) according to literature [18,19]. Methanesulfonic acid ($MeSO_3H$, Janssen Chimica, 99%), TREN (Acros, 96%), decane (Acros, 99+%), toluene (Fischer scientific, HPLC), acetone (Fischer scientific, HPLC), methyl-2-bromopropionate (MBP, Aldrich, 98%), ethyl acetate (Fischer scientific, HPLC) and aluminium oxide (Aldrich, neutral, activated, 58 Å) were used as received. For dialysis, spectra/por 7 (MWCO 1000) membranes from spectrum laboratories were used.

2.2. Characterization

^{1}H NMR spectra were recorded on a Bruker AM500 or Bruker Avance 300 spectrometer, and were measured in $CDCl_3$ (P*t*BuA/P2EHA copolymers) or THF-d_8 (PAA/P2EHA copolymers) at room temperature.

Gel permeation chromatography (GPC) for P*t*BuA/P2EHA copolymers was performed on a Waters 150-C at 35 °C, equipped with Styragel HT3 and HT4 columns. PS standards were used for calibration with $CHCl_3$ as eluent at a flow rate of 1.0 ml/min. PAA/P2EHA copolymers were measured on three serial mixed-B columns from Polymer Labs at 40 °C using a refractive index detector (2410 Waters). PS standards were used for calibration with *N*,*N*-dimethylacetamide (DMA) + 0.21% LiCl + 0.63% HOAc as eluent at a flow rate of 1.0 ml/min.

Gas chromatography was performed on a GC8000 from CE instruments with a DB-5MS column (60 m × 0.249 mm × 0.25 μm) from J & W scientific. Detection was done with an FID-detector. Injector and detector temperatures were kept constant at 250 °C. The column was initially set at 50 °C for 3 min, followed by a heating rate of 20 °C/min until 230 °C and kept for 8 min at this temperature. Conversion was determined by using ethyl acetate or decane as internal standard.

MALDI-TOF MS spectra were recorded with a PerSeptive Biosystems Voyager-DE STR MALDI-TOF MS spectrometer equipped with 2 m linear and 3 m reflector flight tubes and a 337 nm nitrogen laser (3 ns pulse). All mass spectra were obtained with an accelerating potential of 20 kV in positive ion and reflector mode with delayed extraction. Data were processed with Voyager software. For P2EHA, dithranol (20 mg/ml THF) was used as a matrix and sodium trifluoroacetate (NaTFA) (1 mg/ml THF) as cationating agent. Polymer samples were dissolved in THF (1 mg/ml THF). Matrix, salt and polymer were mixed at a 1:1:1 volume ratio before being spotted.

2.3. ATRP of 2-ethylhexyl acrylate (2EHA) with methyl-2-bromopropionate as initiator

A typical procedure for the ATRP of 2EHA (theoretical degree of polymerization 40) is as follows: 2EHA (7.5 ml, 6.64 g, 0.0360 mol), ethyl acetate (100 wt% compared to amount of monomer and ligand, 6.79 g, 7.53 ml), and ligand (for PMDETA: 100 mol% compared to initiator, 0.900 mmol, 0.156 g, 0.188 ml; for Me_6–TREN: 25 mol% compared to initiator, 0.225 mmol, 0.0518 g, 0.0597 ml) are mixed together in a two-neck flask. The solution is purged with nitrogen flow for at least 30 min; then CuBr is added (100 mol% compared to ligand, for PMDETA: 0.900 mmol, 0.129 g; for Me_6–TREN: 0.225 mmol, 0.0323 g). The solution is stirred for an additional 15 min (turns green) and heated to reaction temperature in an oil bath or double jacketed reactor, after which the initiator methyl-2-bromopropionate (0.900 mmol, 0.150 g, 0.100 ml) is added dropwise. Samples were withdrawn for GC (to determine conversion) and GPC (to determine the average number molecular weight (M_n) and polydispersity). The reaction was stopped by cooling to room temperature, adding an excess of ethyl acetate and stirring under air. The catalyst was removed by filtration over neutral aluminium oxide, the solvent was evaporated and the P2EHA was redissolved in acetone and precipitated three times in an MeOH/H_2O (80/20 v/v) mixture to remove the remaining monomer and solvent. Composition was determined by ^{1}H NMR.

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 0.72–1.0 (broad, 6H, $C_2H_3COOC_2H_3(CH_2C\boldsymbol{H}_3)C_3H_6C\boldsymbol{H}_3$), 1.17–1.40 (broad, 8H, $C_2H_3COOC_2H_3(C\boldsymbol{H}_2CH_3)C_3\boldsymbol{H}_6CH_3$), 1.40–2.10 (broad, 3H, $C\boldsymbol{H}_2CHCOOCH_2C\boldsymbol{H}(C_2H_5)C_4H_9$), 2.10–2.62 (broad, 1H, $CH_2C\boldsymbol{H}COOCH_2CH(C_2H_5)C_4H_9$), 3.72–4.27 (broad, 2H, $C_2H_3COOC\boldsymbol{H}_2CH(C_2H_5)C_4H_9$), 3.61–3.66 (s, 3H, methyl group initiator).

2.4. *ATRP of tert-butyl acrylate (tBuA) with methyl-2-bromopropionate as initiator*

A typical procedure for the ATRP of *t*BuA (theoretical degree of polymerization 20) is as follows: *t*BuA (10 ml, 8.75 g, 0.0683 mol), toluene (70 wt% compared to *t*BuA, 6.13 g, 7.08 ml), acetone (20 wt% compared to *t*BuA, 1.75 g, 2.21 ml), decane (10 wt% compared to *t*BuA, 0.875 g, 1.20 ml) and Me_6–TREN (5 mol% compared to initiator, 0.171 mmol, 0.0393 g, 45.2 µl) are mixed together in a two-neck flask. The solution is purged with nitrogen flow for at least 30 min after which CuBr is added (5 mol% compared to initiator, 0.171 mmol, 0.0245 g). The solution is stirred for an additional 15 min (turns light green) and heated to reaction temperature in an oil bath after which the initiator methyl-2-bromopropionate (3.41 mmol, 0.570 g, 0.381 ml) is added dropwise. Samples were withdrawn for GC (to determine conversion, decane as internal standard) and GPC. The reaction was stopped by cooling to room temperature, adding an excess of acetone and stirring under air. The catalyst was removed by filtration over neutral aluminium oxide, the solvent was evaporated and the sticky P*t*BuA was dried in a vacuum oven as a thin film at 40 °C for 48 h to remove the remaining solvent and monomer. Composition was determined by ^{1}H NMR.

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 1.3–2 (broad, 11H, $C\boldsymbol{H}_2$ and $C(C\boldsymbol{H}_3)_3$ protons of P*t*BuA), 2.25 (broad, 1H, $C\boldsymbol{H}$ protons of P*t*BuA), 3.65 (s, 3H, methylester initiator), 4.11 (m, 1H, $R_2C\boldsymbol{H}Br$).

2.5. *Synthesis of PtBuA-b-P2EHA with PtBuA macroinitiator*

A typical procedure for the ATRP of 2EHA from a P*t*BuA macroinitiator (theoretical degree of polymerization 11) is as follows: P*t*BuA (DP = 23.1, 30 g, 9.58 mmol), 2EHA (21.95 ml, 19.43 g, 0.1054 mol), ethyl acetate (100 wt% compared to amount of monomer and macroinitiator, 49.43 g, 54.86 ml), and ligand (for PMDETA: 80 mol% compared to initiator, 7.66 mmol, 1.33 g, 1.60 ml; for Me_6–TREN: 5 mol% compared to initiator, 0.479 mmol, 0.110 g, 0.127 ml) are mixed together in a two-neck flask. The solution is purged with nitrogen flow for at least 30 min after which CuBr is added (100 mol% compared to ligand, for PMDETA: 7.66 mmol, 1.10 g; for Me_6–TREN: 0.479 mmol, 0.0687 g). The solution is stirred for an additional 15 min (turns green) and then heated to reaction temperature in a double jacketed reactor. Samples were withdrawn for GC and GPC. The reaction was stopped by cooling to room temperature, adding an excess of ethyl acetate and stirring under air. The catalyst was removed by filtration over neutral aluminium oxide and the solvent and monomer were evaporated under reduced pressure. Composition was determined by ^{1}H NMR.

2.6. *Synthesis of P2EHA-b-PtBuA with P2EHA macroinitiator*

A typical procedure for the ATRP of *t*BuA from a P2EHA macroinitiator (theoretical degree of polymerization 60) is as follows: P2EHA (DP = 27, 10 g, 2.083 mmol), *t*BuA (18.31 ml, 16.02 g, 0.125 mol), ethyl acetate (50 wt% compared to amount of monomer and macroinitiator, 13.01 g, 14.42 ml) and PMDETA (100 mol% compared to initiator, 2.083 mmol, 0.361 g, 0.435 ml) are mixed together in a two-neck flask. The solution is purged with nitrogen flow for at least 30 min after which CuBr is added (100 mol% compared to ligand, 2.083 mmol, 0.299 g). From here, the same procedure was followed as for the block copolymerization of P*t*BuA with 2EHA.

2.7. *Synthesis of random copolymers of tBuA and 2EHA via ATRP*

A typical procedure for the random copolymerization of *t*BuA with 2EHA (theoretical degree of polymerization 17 for both monomers) via ATRP is as follows: 2EHA (28.43 ml, 25.16 g, 0.1365 mol), *t*BuA (20 ml, 17.5 g, 0.1365 mol), ethyl acetate (100 wt% compared to amount of monomer, 42.66 g, 47.29 ml) and PMDETA (100 mol% compared to initiator, 8.03 mmol, 1.392 g, 1.68 ml) are mixed together. The solution is purged with nitrogen flow for at least 30 min after which CuBr is added (100 mol% compared to ligand, 8.03 mmol, 1.152 g). The solution is stirred for an additional 15 min (turns green) and then heated to reaction temperature in a double jacketed reactor after which the initiator methyl-2-bromopropionate (8.03 mmol, 1.341 g, 0.896 ml) is added dropwise. From here, the same procedure was followed as for the block copolymerization of P*t*BuA with 2EHA.

2.8. *Synthesis of ''blocky'' gradient copolymers of tBuA and 2EHA via ATRP*

A typical ''blocky'' gradient copolymerization of *t*BuA and 2EHA (theoretical degree of polymerization 15 for *t*BuA, 17 for 2EHA) is as follows: *t*BuA (20 ml, 17.5 g, 0.1365 mol), ethyl acetate (100 wt% compared to amount of *t*BuA, 17.5 g, 19.4 ml) and PMDETA (100 mol% compared to initiator, 9.10 mmol, 1.577 g, 1.900 ml) are mixed together in a double jacketed reactor. The solution is purged with nitrogen flow for at least 30 min after which CuBr is added (100 mol% compared to ligand, 9.10 mmol, 1.306 g). The solution is stirred for an additional 15 min (turns green) and then heated to reaction temperature in a double jacketed reactor. Samples were withdrawn for GC (to determine conversion) and GPC (to determine M_n and polydispersity). After reaching a desired conversion, a mixture of 2EHA (32.22 ml, 28.52 g, 0.1547 mol) and ethyl acetate (100 wt% compared to amount of 2EHA, 28.5 g, 31.6 ml), purged with N_2, was added to the reaction solution. From here, the same procedure was followed as for the block copolymerization of P*t*BuA with 2EHA.

2.9. Hydrolysis of PtBuA in copolymers with P2EHA

A 10 wt% solution of the P*t*BuA/P2EHA copolymers was made in CH_2Cl_2. After dissolving, $MeSO_3H$ (150 mol%, compared to the total amount of *t*BuA groups in the copolymer) was added and the reaction was stirred for 1 h at room temperature. While PAA precipitates in such conditions, the PAA-containing copolymers remained in solution because of the presence of P2EHA. After 1 h, THF was added and $MeSO_3H$ was neutralized with $NaHCO_3$ until the formation of CO_2 stopped. Precipitated salts were filtered off and the solvent was evaporated. Characterization of the PAA/P2EHA copolymers was done by GPC and ^{1}H NMR (in THF-d_8).

3. Results and discussion

3.1. Homopolymerization of 2EHA by ATRP

As mentioned in Section 1, the controlled polymerization of 2EHA by ATRP has not yet been demonstrated in the available literature [15,16]. On the other hand, the ATRP of other types of acrylates has already been described in numerous papers [20–23] and is therefore well known. For the synthesis of P2EHA, reaction conditions similar to those of other acrylates have been chosen. CuBr was used as the transition metal, MBP as initiator and PMDETA or Me$_6$–TREN as ligands [24–26]. Ethyl acetate was chosen as solvent because it is considered to be an ecologically friendly solvent. To prove that these reaction conditions result in controlled ATRP, first order kinetics and the evolution of molecular weight as a function of conversion were investigated. At the same time, the reproducibility was tested by repeating each reaction twice for both ligands. Four reactions were carried out (1/A1, 1/A2, 1/B1 and 1/B2) with reaction conditions as described in Table 1. First order kinetics and evolution of molecular weight and polydispersity vs conversion are given in Figs. 1 and 2.

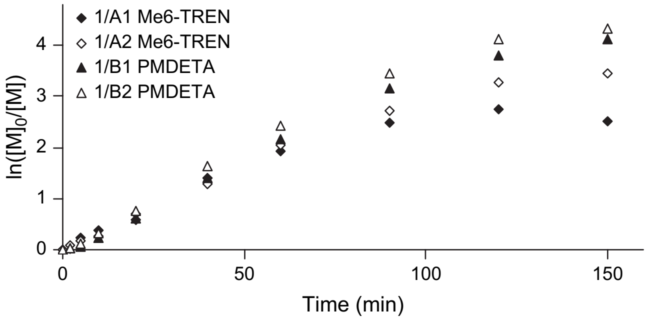

Fig. 1. Kinetic plot of ln([M]$_0$/[M]) vs reaction time for ATRP of 2EHA with Me$_6$–TREN (1/A1 ◆ and 1/A2 ◇) or PMDETA (1/B1 ▲ and 1/B2 △); [2EHA]/[MBP]/[CuBr]$_0$/[Me$_6$–TREN] = 40/1/0.25/0.25 and [2EHA]/[MBP]/[CuBr]/[PMDETA] = 40/1/1/1; 70 °C in 100 wt% ethyl acetate.

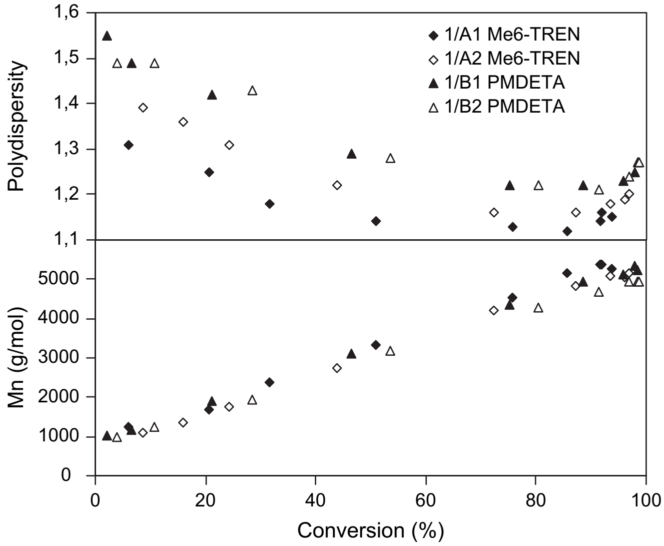

Fig. 2. Polydispersity vs conversion and molecular weight vs conversion for ATRP of 2EHA with Me$_6$–TREN (1/A1 ◆ and 1/A2 ◇) or PMDETA (1/B1 ▲ and 1/B2 △); [2EHA]/[MBP]/[CuBr]/[Me$_6$–TREN] = 40/1/0.25/0.25 and [2EHA]/[MBP]/[CuBr]/[PMDETA] = 40/1/1/1; 70 °C in 100 wt% ethyl acetate.

The first order kinetic plot (Fig. 1), in combination with the evolution of the molecular weight as a function of conversion (Fig. 2), shows that the reactions are controlled for at least 90 min. At this point, the conversions are already exceeding 90%. At high conversions, the polymerizations with Me$_6$–TREN as the ligand (1/A1 and 1/A2) start to slow down due to termination reactions. The polymerization reactions with PMDETA (1/B1 and 1/B2) are controlled for a longer period,

Table 1
Synthesis of homopolymers of 2-ethylhexyl acrylate by ATRP

Exp.[a]	Ligand	[I]$_0$/[CuBr]$_0$/[ligand]$_0$	Time (min)	Conversion (%)[b]	$M_{n,th}$[c] (g/mol)	$M_{n,GPC}$[d] (g/mol)	M_w/M_n[d]
1/A1	Me$_6$–TREN	1/0.25/0.25	150	92	6950	5360	1.16
1/A2	Me$_6$–TREN	1/0.25/0.25	150	97	7320	5150	1.20
1/B1	PMDETA	1/1/1	150	98	7390	5250	1.27
1/B2	PMDETA	1/1/1	150	99	7460	4950	1.27
1/C1[e]	Me$_6$–TREN	1/0.25/0.25	50	56	4320	3020	1.16

[a] [M]$_0$/[I]$_0$ = 40, T = 70 °C, solvent = ethyl acetate (100 wt% compared to monomer + ligand), initiator = methyl-2-bromopropionate.
[b] Determined by GC.
[c] $M_{n,th}$ = 167 (MM MBP) + conversion × 40 × 184.28 (MM 2EHA).
[d] GPC with $CHCl_3$ as eluent and PS standards.
[e] DP = 27 (calculated by ^{1}H NMR, comparison between integrations protons C and K, Fig. 3).

but after 120 min (conversion ~ 98%), a deviation from first order kinetics is also observed. The side reactions, responsible for the slower kinetics, are also responsible for the increase in polydispersity at high conversions (>90%). At a conversion of about 85%, PDIs in the range of 1.1 (Me_6–TREN) and 1.2 (PMDETA) can be observed (Fig. 2). In spite of the linearity of M_n vs conversion plot and the low polydispersities, a small number of chain transfer reactions via abstraction of a hydrogen atom from tertiary carbons of the polymer backbone, typically for poly(acrylate)s, cannot be excluded as will be discussed below for the MALDI-TOF analysis [27,28].

Since the reactions with Me_6–TREN always result in lower PDI compared to PMDETA, this ligand was chosen for the synthesis of a larger quantity of P2EHA macroinitiator for block copolymerizations with *t*BuA. The use of Me_6–TREN is also preferred as much less CuBr is used in comparison to the reactions with PMDETA. The results for this batch reaction are mentioned in Table 1 (reaction 1/C1, DP = 27). The polymer, obtained at 56% conversion, was purified by precipitation in an 80/20 MeOH/H_2O mixture (three times) to remove all monomers. Since P2EHA has a low T_g (~−50 °C) [29], a sticky polymer was obtained.

While the degree of polymerization can be derived from ^1H NMR analysis (Fig. 3), the end group functionality could not be calculated accurately because there is a partial overlap between a polymer peak (protons C) and the peak from the hydrogen next to the bromine (proton L). Therefore, MALDI-TOF MS was carried out onto the purified polymer batch 1/C1 (Fig. 4).

The spectrum mostly shows the expected peaks of P2EHA initiated by MBP with a bromine end group. Upon comparison between the experimental and theoretical distributions (Fig. 4b), only minor side peaks were detected. Quantitative determination of the fractions of all signals is not possible with MALDI-TOF. One of the small side distributions originates from the replacement of a bromine by a hydrogen (Fig. 4a), which occurred during the reaction (not observable in NMR spectra). Bednarek et al. described earlier similar side series, which were attributed to the exchange of a hydrogen from the ligand PMDETA with the Br-end group from the polymer [30]. This transfer reaction might explain the small discrepancy of the experimental M_n-value (3840 g/mol,

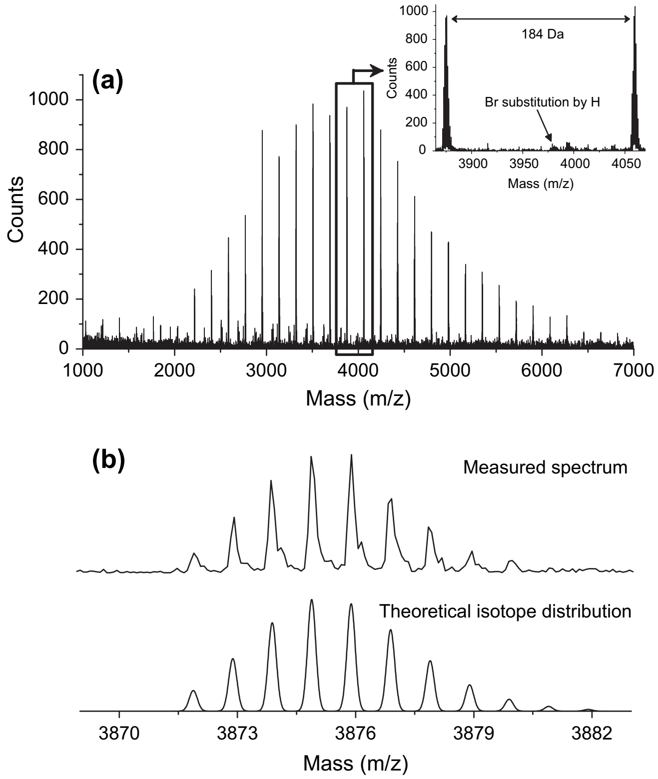

Fig. 4. Reflector MALDI-TOF MS spectrum of P2EHA 1/C1 in dithranol with NaTFA (a) complete spectrum and inset of 3860–4070 Da (b) comparison of measured isotope distribution (top) and theoretical isotope distribution (bottom).

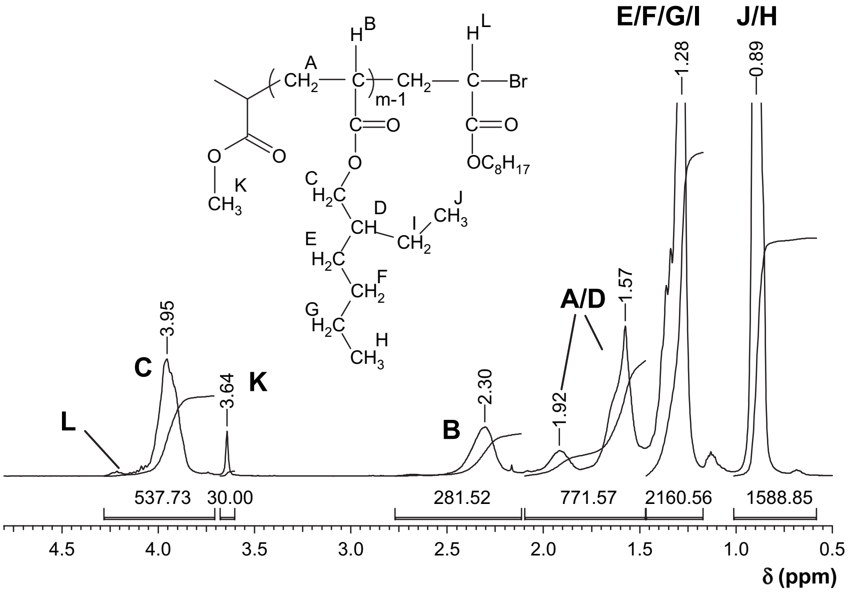

Fig. 3. ^1H NMR spectrum ($CDCl_3$) of P2EHA after precipitation in 80/20 MeOH/H_2O mixture and drying.

obtained by MALDI-analysis) with the theoretical M_n (4320 g/mol, Table 1). Side peaks originating from a substitution reaction by H_2O or MeOH, used to precipitate the polymer, were not detected. Also, series that correspond to polymers with two or more Br-end groups as a result of intermolecular chain transfer reactions are not detected. It was already shown by Charleux [27] and others that the chain transfer mechanism of polyacrylates seems to be predominantly an intramolecular process (presumably backbiting). As the intramolecular chain transfer process does not change the chain composition and hence the molar mass and end group functionality, the MALDI-analysis could not detect the corresponding branched products. It has been shown earlier by detailed ^{13}C NMR analysis of poly(*n*-butylacrylate) that a small fraction of branches (lower than 3%) could indeed be identified in certain conditions [27]. Although a detailed ^{13}C NMR analysis was out of the scope of this investigation, the narrow polydispersities and the kinetic analysis support the idea that only a small amount of branches could be present if the conversion is not too high. From these observations, it can be concluded that the end group functionality is high and that the P2EHA macroinitiator should be suitable for block copolymerizations.

3.2. Block copolymerization of P2EHA with tBuA by ATRP

The above synthesized macroinitiator P2EHA (reaction 1/C1, Table 1) was used to initiate the polymerization of *t*BuA (Table 2). Ethyl acetate was used as solvent with CuBr/PMDETA as catalyst. Different lengths for the P*t*BuA block were targeted, ranging from DP 25 to 100. This corresponds to a percentage of P*t*BuA in the block copolymer ranging from 48 to 79%. Since the P*t*BuA-segments will be converted into PAA, a high content is important to investigate the water solubility behaviour of the P2EHA-*b*-PAA structures in a later stage.

All three block copolymerizations resulted in the formation of block copolymers with narrow polydispersities. GPC results (Fig. 5) show that the initiation efficiency of P2EHA is high, but not quantitative: a small amount of macroinitiator does not react and is visible as a small tailing, especially for reactions 2/A1 (curve d) and 2/B1 (curve c). This tailing is ascribed to the presence of unfunctionalized P2EHA (no bromine end group), which was noticed in the MALDI-TOF MS spectrum (Fig. 4). In order to avoid the presence of homopolymers, the reverse way to synthesize these block copolymers was attempted: the polymerization of *t*BuA as the first step, and then using the P*t*BuA macroinitiator for ATRP of 2EHA.

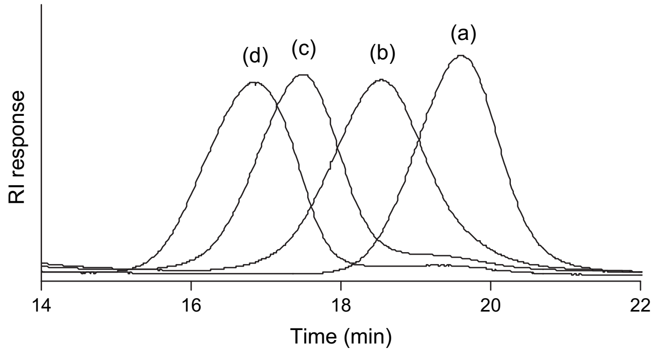

Fig. 5. GPC traces (RI detection) of (a) P2EHA macroinitiator (1/C1), (b) P2EHA-*b*-P*t*BuA (entry 2/C1, Table 2), (c) P2EHA-*b*-P*t*BuA (entry 2/B1, Table 2) and (d) P2EHA-*b*-P*t*BuA (entry 2/A1, Table 2).

3.3. Block copolymerization of PtBuA with 2EHA by ATRP

The homopolymerization of *t*BuA was performed in a mixture of toluene/acetone/decane 70/20/10 wt% (decane as internal standard for GC). This method has been reported earlier and resulted already in numerous well-defined macroinitiators [14]. Therefore, a batch of the macroinitiator was synthesized immediately (reaction 3/A1, Table 3), without prior kinetic studies. CuBr was used as catalyst in combination with Me_6–TREN. Although only 5% catalyst was added (compared to the initiator), the polymerization occurred in a fast manner.

As reported in Table 3, a well-defined macroinitiator with narrow polydispersity index (1.09) and a DP of around 52 was obtained. Compared to the amount of incorporated initiator, the Br-end group functionality is about 90% as calculated from ^{1}H NMR. This indicates that, just as for P2EHA, small loss of Br-end groups can occur during the reaction. It was observed earlier that also termination reactions, especially occurring during the start of the polymerization, can account for this incomplete functionalization, even at low monomer conversions.

With the P*t*BuA macroinitiator, several block copolymerizations were performed with 2EHA. For the P2EHA segment, four DPs of 100, 70, 50 and 10, respectively were targeted (Table 3), resulting in a P*t*BuA-content ranging from 34 to

Table 2
Synthesis of block copolymers of P2EHA with *t*-butyl acrylate by ATRP

Exp.[a]	$[M]_0/[I]_0/[CuBr]_0/[ligand]_0$	Time (min)	Conversion (%)[b]	$M_{n,th}$[c] (g/mol)	$M_{n,NMR}$[d] (g/mol)	$M_{n,GPC}$[e] (g/mol)	M_w/M_n[e]	DP P2EHA-*b*-P*t*BuA[d]	P*t*BuA[d] (mol%)
2/A1	120/1/1/1	420	75	16,690	18,250	12,790	1.28	27-*b*-99	79
2/B1	60/1/1/1	180	86	11,760	13,810	9080	1.22	27-*b*-56	67
2/C1	25/1/1/1	75	94	8160	8440	5500	1.20	27-*b*-25	48

[a] $T = 70$ °C, ligand = PMDETA, solvent = ethyl acetate (50 wt% compared to monomer + initiator), initiator = P2EHA 1/C1.
[b] Determined by GC.
[c] $M_{n,th} = 167$ (MM MBP) + (27 (DP P2EHA) × 184.28) + conversion × $[M]_0/[I]_0$ × 128.17 (MM *t*BuA).
[d] Determined by ^{1}H NMR.
[e] GPC with $CHCl_3$ as an eluent and PS standards.

Table 3
Synthesis of block copolymers of P*t*BuA with 2-ethylhexyl acrylate by ATRP

Exp.	$[M]_0/[I]_0/[CuBr]_0/[ligand]_0$	Time (min)	Conversion (%)[c]	$M_{n,th}$[d] (g/mol)	$M_{n,NMR}$[e] (g/mol)	$M_{n,GPC}$[f] (g/mol)	M_w/M_n[f]	DP[e]	P*t*BuA[e] (mol%)
3/A1[a]	60/1/0.05/0.05	120	82	6470	6830	6270	1.09	52	100
4/A1[b]	120/1/0.8/0.8	240	92	27,180	25,260	19,650	1.23	52-*b*-100	34
4/B1[b]	120/1/0.8/0.8	400	67	21,650	19,180	12,190	1.22	52-*b*-67	44
4/C1[b]	65/1/0.8/0.8	360	79	16,290	14,940	9460	1.24	52-*b*-44	54
4/D1[b]	13/1/0.8/0.8	70	78	8700	8670	6330	1.19	52-*b*-10	84

[a] $T = 60$ °C, solvent = toluene/acetone/decane 70/20/10 (100 wt% compared to monomer), initiator = MBP.

[b] $T = 80$ °C, ligand = PMDETA, initiator = P*t*BuA 3/A1, solvent = ethyl acetate (4/B1, 4/C1, 4/D1: 100 wt% compared to monomer + P*t*BuA; 4A1: 33 wt%).

[c] Determined by GC.

[d] $M_{n,th} = 167$ (MM MBP) + (52 (DP P*t*BuA) × 128.17) + conversion × $[M]_0/[I]_0$ × 184.28 (MM 2EHA).

[e] Determined by ^1H NMR.

[f] GPC with $CHCl_3$ as an eluent and PS standards.

84%. The reactions were performed with PMDETA/CuBr as the catalyst and ethyl acetate as solvent.

All the four reactions yield block copolymers with narrow polydispersities and a P2EHA segment in the desired molecular weight range. The GPC results (Fig. 6) show a more quantitative initiation by the P*t*BuA macroinitiator as compared to the results obtained with the P2EHA initiator (Fig. 5). Even for the block copolymers with the highest amount of P2EHA (curve e), no remaining signal of the macroinitiator was observed.

3.4. Random copolymerization of tBuA and 2EHA by ATRP

Besides the synthesis of block copolymers consisting of P*t*BuA and P2EHA, the preparation of the corresponding well-defined random copolymers has been investigated. Such structures are prepared via a one-pot synthesis, by mixing the two monomers and polymerizing them by ATRP. The randomness of the obtained copolymers depends on the copolymerization parameters of both monomers. For other examples of copolymerizations of two acrylates, copolymerization parameters close to 1 have been reported [29]. Three copolymerizations were carried out in ethyl acetate starting from different monomer ratios ($[tBuA]_0/[2EHA]_0 = 1/1$, 1.66/1 and 2/1) (Table 4).

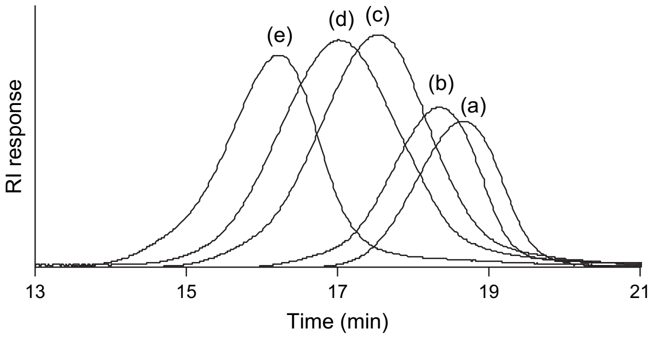

Fig. 6. GPC traces (RI detection) of (a) P*t*BuA macroinitiator (3/A1, Table 3), (b) P*t*BuA-*b*-P2EHA (entry 4/D1, Table 3), (c) P*t*BuA-*b*-P2EHA (entry 4/C1, Table 3), (d) P*t*BuA-*b*-P2EHA (entry 4/B1, Table 3) and (e) P*t*BuA-*b*-P2EHA (entry 4/A1, Table 3).

For reaction 5/A1, a kinetic study was carried out, by taking samples for GC and GPC at regular time intervals, to determine if the random copolymerization was controlled and at which rate the two monomers were consumed.

As can be observed from Fig. 7a, both monomers are incorporated at about the same rate. There is an almost exact overlap between the data points of conversions for both monomers. Moreover, the evolution of molecular weight vs conversion (Fig. 7b) is linear. In this way, three random copolymers were synthesized in a controlled manner, with a P*t*BuA-content ranging from 50 to 67%.

3.5. Synthesis of blocky gradient copolymers of tBuA and P2EHA by ATRP

Finally, the so-called "blocky" gradient copolymers based on *t*BuA and 2EHA have been prepared [31]. These are copolymers that start with a block segment, followed by a copolymer segment that contains both monomers. Recently, it has been demonstrated that such blocky gradient structures can act as efficient compatibilizer for polymer blends, even better than

Table 4
Synthesis of random copolymers of 2EHA and *t*BuA by ATRP

Exp.[a]	$[tBuA]_0/[2EHA]_0/[I]_0$	Time (min)	Conversion *t*BuA (%)[b]	Conversion 2EHA (%)[b]	$M_{n,th}$[c] (g/mol)	$M_{n,NMR}$[d] (g/mol)	$M_{n,GPC}$[e] (g/mol)	M_w/M_n[e]	DP P*t*BuA-*co*-P2EHA[d]	P*t*BuA[d] (mol%)
5/A1	17/17/1	225	85	84	4650	4850	4950	1.13	15-*co*-15	50
5/B1	30/18/1	285	83	81	6050	7020	5790	1.15	29-*co*-17	63
5/C1	24/12/1	210	95	94	5170	5450	4630	1.14	24-*co*-12	67

[a] $T = 50$ °C, $[I]_0/[CuBr]_0/[PMDETA] = 1/1/1$, initiator = MBP, solvent = ethyl acetate (100 wt% compared to monomer).

[b] Determined by GC.

[c] $M_{n,th} = 167$ (MM MBP) + $[tBuA]_0/[I]_0$ × conversion *t*BuA × 128.17 + $[2EHA]_0/[I]_0$ × conversion 2EHA × 184.28.

[d] Determined by ^1H NMR.

[e] GPC with $CHCl_3$ as an eluent and PS standards.

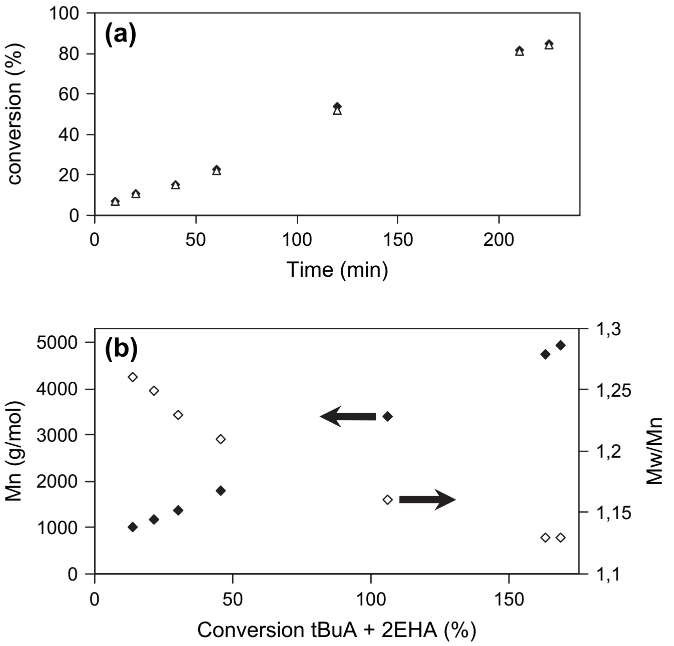

Fig. 7. Kinetic plots of (a) conversion vs reaction time (*t*BuA ◆ and 2EHA △) and (b) molecular weights (◆) and molecular weight distributions (◇) vs monomer conversion for the ATRP of *t*BuA and 2EHA with [*t*BuA]/[2EHA]/[MBP]/[CuBr]/[PMDETA] = 17/17/1/1/1 in 100 wt% ethyl acetate at 50 °C.

block copolymers [32]. For the preparation, *t*BuA was first polymerized until a certain conversion, after which 2EHA was added. This procedure leads to copolymers that consist of a P*t*BuA segment, followed by a random structure of both monomers with high 2EHA-content. In order to obtain blocky gradient copolymers with equal structure and composition for each chain, the initially formed P*t*BuA-segments should initiate the *t*BuA/2EHA mixture after addition of 2EHA. In Table 5, an overview is given of the experimental data obtained with the blocky gradient structures, respectively with PMDETA and Me_6−TREN as ligand. For all reactions, CuBr was used as catalyst, MBP as initiator and ethyl acetate as solvent.

The first two reactions only differ in conversion of *t*BuA before adding 2EHA (at 74 and 94%, respectively). Especially for the second case, a ‘‘blocky’’ structure is obtained for the whole copolymer. This is reflected in the composition of the final structure, P(*t*BuA$_{14}$//*t*BuA$_1$/2EHA$_{14}$), which indicates that only one *t*BuA unit is incorporated after the addition of the second monomer. For this second reaction, GPC curves of the structures before adding 2EHA and at the end of the copolymerization are shown in Fig. 8.

From the GPC-analysis, it could be concluded that the P*t*BuA-segments provided efficient initiation for the second, more random segment, even though the conversion had already reached 94% at that time. In this way, it is possible to synthesize structures that resemble block copolymers. The advantage of this synthetic approach is that time-consuming purification reactions are avoided and replaced by a one-pot synthesis.

The third gradient copolymer (reaction 6/C1) was synthesized with Me_6−TREN as ligand. As the polydispersity is higher than those obtained with PMDETA (1.22 ↔ 1.12), it is recommended to use PMDETA as ligand for the preparation of these blocky gradient copolymers.

3.6. Hydrolysis of PtBuA and solubility behaviour of several types of copolymers

After purification, all of the above-mentioned P*t*BuA containing copolymers were hydrolyzed and their solubility behaviour in slightly basic water (pH ∼ 9) was investigated. Hydrolysis was performed in dichloromethane for 1 h. $MeSO_3H$ was added as a strong acid ($pK_a \sim -2$). The degree of hydrolysis was checked with ^1H NMR in THF-d_8 (Fig. 9).

The NMR spectrum from the hydrolyzed product clearly shows the complete disappearance of the *t*-butyl group. This means that the hydrolysis of P*t*BuA to PAA is quantitative as well as fast. A list of the hydrolyzed copolymers with their composition and other molecular properties is given in Table 6. To make sure that the hydrolysis reaction did not degrade the copolymers, GPC-analysis was conducted. PAA-containing copolymers are often difficult to characterize by GPC because of their interaction with the column. Adler et al. recently reported conditions to overcome these problems [33]. Based on these results, GPC-analysis was carried out in dimethylacetamide (DMA) containing 0.63% acetic acid and

Table 5
Synthesis of ‘‘blocky’’ gradient copolymers of *t*BuA and 2EHA by ATRP

Exp.[a]	$[tBuA]_0/[2EHA]_0/[I]_0$	Ligand	Conversion *t*BuA when adding 2EHA (%)[b]	Conversion *t*BuA (%)[b]	Conversion 2EHA (%)[b]	Total reaction time (min)	$M_{n,th}$[c] (g/mol)	$M_{n,NMR}$[d] (g/mol)	$M_{n,GPC}$[e] (g/mol)	M_w/M_n[e]	DP P*t*BuA-grad-P2EHA[d,f]	P*t*BuA[d] (mol%)
6/A1	15/17/1	PMDETA	74	98	81	270	4590	5220	4840	1.12	P(*t*BuA$_{11}$//*t*BuA$_4$/2EHA$_{17}$)	47
6/B1	15/17/1	PMDETA	94	99	74	330	4390	4670	4490	1.12	P(*t*BuA$_{14}$//*t*BuA$_1$/2EHA$_{14}$)	53
6/C1	20/10/1	Me_6−TREN	14	93	91	360	4230	4260	3720	1.22	P(*t*BuA$_3$//*t*BuA$_{16}$/2EHA$_9$)	66

[a] $T = 50\,°C$, $[I]_0/[CuBr]_0/[PMDETA] = 1/1/1$, $[I]_0/[CuBr]_0/[Me_6{-}TREN] = 1/0.05/0.05$, initiator = MBP, solvent = ethyl acetate (100 wt% compared to monomer).

[b] Determined by GC.

[c] $M_{n,th} = 167$ (MM MBP) + $[tBuA]_0/[I]_0 \times$ conversion *t*BuA × 128.17 + $[2EHA]_0/[I]_0 \times$ conversion 2EHA × 184.28.

[d] Determined by ^1H NMR.

[e] GPC with $CHCl_3$ as an eluent and PS standards.

[f] Notation ‘‘blocky’’ gradients: before double line P*t*BuA segment with average DP; after double line, composition second segment after adding 2EHA.

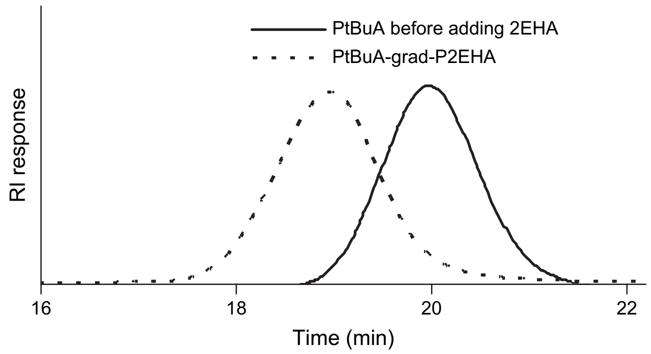

Fig. 8. GPC traces (RI detection) of P*t*BuA before addition of 2EHA (full line) and P*t*BuA-grad-P2EHA at the end of the reaction (dotted line).

Table 6
Hydrolysis of P*t*BuA containing block, random and gradient copolymers

Exp.[a]	Product	DP PAA/P2EHA[b]	Amount PAA (%)[b]	M_n (g/mol)[c]	M_w/M_n[c]
1	P2EHA-*b*-PAA	27-*b*-99	79	19,920	1.30
2	P2EHA-*b*-PAA	27-*b*-56	67	13,520	1.25
3	P2EHA-*b*-PAA	27-*b*-25	48	8200	1.18
4	PAA-*b*-P2EHA	52-*b*-10	84	14,710	1.11
5	PAA-*b*-P2EHA	52-*b*-44	54	12,860	1.18
6	PAA-*b*-P2EHA	52-*b*-67	44	10,930	1.23
7	PAA-*b*-P2EHA	52-*b*-100	34	7250	1.31
8	PAA-*co*-P2EHA	15-*co*-15	50	8450	1.24
9	PAA-*co*-P2EHA	29-*co*-17	63	9680	1.23
10	PAA-*co*-P2EHA	24-*co*-12	67	8860	1.21
11	PAA-grad-P2EHA	P(tBuA$_{11}$//tBuA$_4$/2EHA$_{17}$)	47	6563	1.37
12	PAA-grad-P2EHA	P(tBuA$_{14}$//tBuA$_1$/2EHA$_{14}$)	53	6750	1.32
13	PAA-grad-P2EHA	P(tBuA$_3$//tBuA$_{16}$/2EHA$_9$)	66	7910	1.20

[a] Copolymer dissolved in 10 wt% H_2O, pH adjusted with concentrated aqueous NaOH.

[b] Determined by ^{1}H NMR on non-hydrolysed precursors.

[c] GPC with DMA + 0.63% HOAc + 0.21% LiCl as eluent and calibrated with PS standards.

0.21% LiCl. As can be seen from the comparison of Table 6 and Tables 2–5, comparable polydispersities are obtained for the copolymers before and after the hydrolysis. This indicates that $MeSO_3H$ did not degrade the copolymers.

Since there is much hydrophobic P2EHA present in the different copolymers, most polymers did not really dissolve in basic water (10 wt% solutions) but form aggregates. As expected, the solubility strongly depends on the PAA-amount and on the copolymer structure. For the block copolymers (entries 1–7, Table 6), aggregate formation is observed above a PAA-content of about 60%. At lower contents, the copolymer is only slightly soluble and below 50%, only longer PAA block lengths result in partial solubility. The exact nature of the aggregates as a function of concentration and PAA-content is now under investigation and out of the scope of this paper.

On the other hand, the random copolymers are much more soluble because the PAA units are distributed along the chain and help to solubilize the P2EHA. Above a PAA ratio of about 2/3, almost no aggregate formation was observed anymore. The gradient copolymers also give better solubility results. Especially, entry 12 is interesting because it has a blocky structure with a PAA-content of 53%, which is comparable to block copolymer 5 with 54% PAA. While the latter one is only slightly soluble, the gradient copolymer is completely soluble. Apparently, the small amount (~6%) of PAA incorporated in the P2EHA segment is enough to solubilize the copolymer

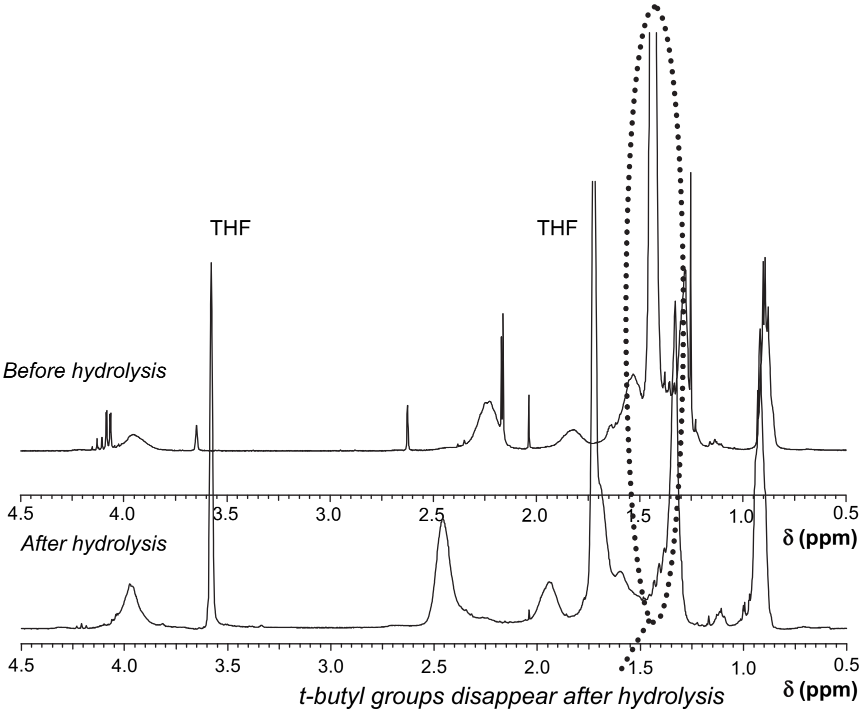

Fig. 9. Comparison of ^{1}H NMR spectra of the P*t*BuA–P2EHA copolymer (in $CDCl_3$, top) and the hydrolysed product PAA–P2EHA (in THF-d_8, bottom).

structure. Although more profound physical studies should be performed, for example with light scattering, for a better understanding of these structure–property relationships, this solubility study already indicates the drastic influence of the microstructure of the copolymer structures on their physical properties.

4. Conclusions

Poly(2-ethylhexyl acrylate) was synthesized in a controlled way by ATRP. Next, it was successfully used as a macroinitiator for *t*BuA and incorporated in block-, random- and blocky gradient copolymers with P*t*BuA. After purification, the P*t*BuA part was hydrolysed with $MeSO_3H$ in a fast and quantitative way, as confirmed by ^1H NMR. Solubility tests in slightly basic water on the hydrolysed samples showed that the solubility depends on the incorporated amount of PAA and on the copolymer structure. In the case of the gradient copolymers, the incorporation of a small amount of PAA in the second segment can drastically alter the solubility behaviour.

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