Electronic Supplementary Information (ESI)

Dixanthate-terminated poly(butylene terephthalate). A novel RAFT/MADIX agent for the synthesis of well-defined triblock copolymers resulting from consecutive step- and chain-growth polymerization

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Summary of the Supplementary Information document

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I. Determination of the experimental conditions of the hydroxybutyl-2-bromopropionate synthesis

The reaction between 1,4-butanediol (BTDiOH) and 2-bromopropionyl bromide has led to the formation of the hydroxybutyl-2-bromopropionate **4** and butyl-dibromopropionate **4’**. A large excess of 1,4-butanediol was necessary to form preferentially the expected compound **4**. The molar ratio between BTDiOH and 2-bromopropionyl bromide was varied to determine the evolution of molar proportion of **4** and **4’**. It was showed that 10 equivalents of 1,4-butanediol were necessary to form more than 80% of compound **4**. There was no significant difference between 20 and 50 equivalents of 1,4-butanediol which led to the formation of **4’** in both cases.

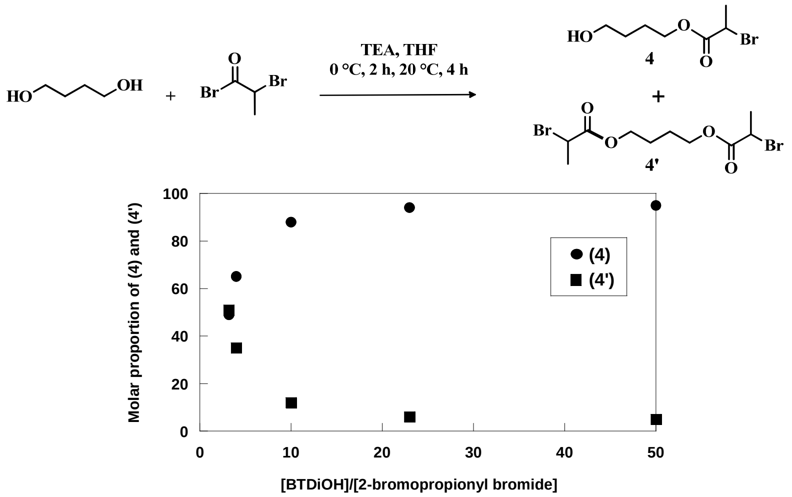

Fig. S1 Evolution of molar proportion of (4) and (4’) with the molar ratio between 1,4-butanediol and 2-bromopropionyl bromide.

II. NMR spectroscopy of dixanthate-terminated PBT$_B$

Xanthate-end-functionalized poly(butylene terephthalate) **3** synthesized by method B was characterized by NMR spectroscopy. Analyses were performed in 1,1,2,2-TCE-*d2* ($C_2D_2Cl_4$) at room temperature after heating for a complete solubilization of the sample. Assignments of ^1H and ^{13}C NMR peaks are similar to compound **3** synthesized by method A.

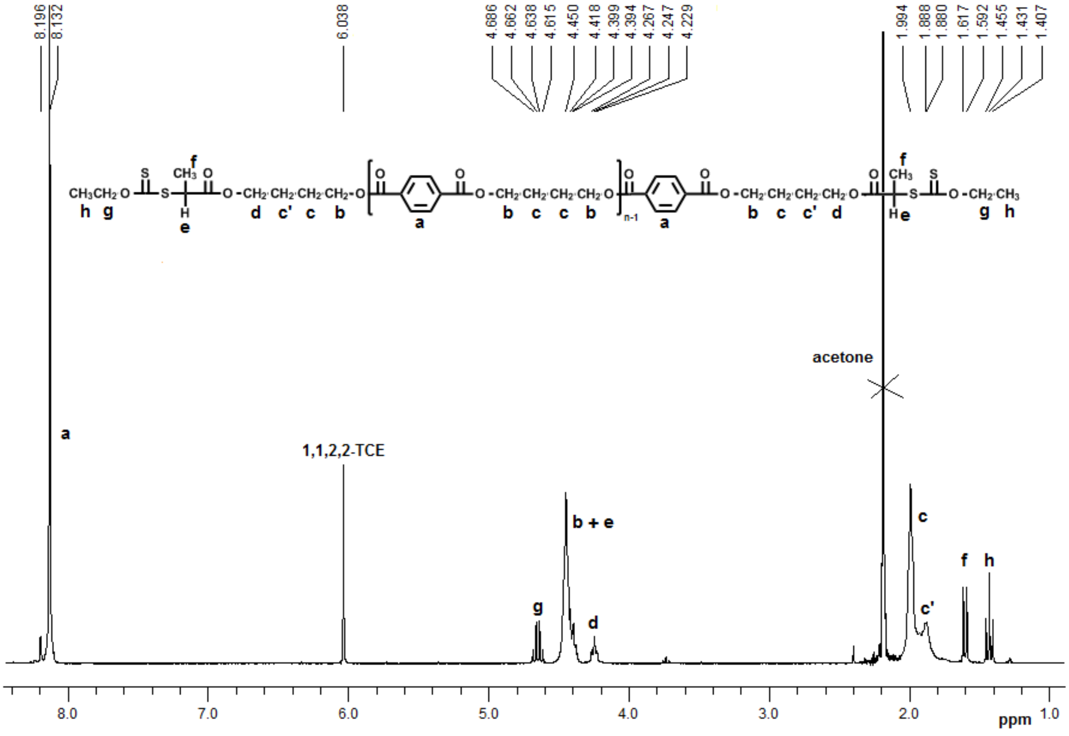

Fig. S2: ^1H NMR spectrum of xanthate-end-functionalized PBT synthesized by method B (P2) with peak assignments.

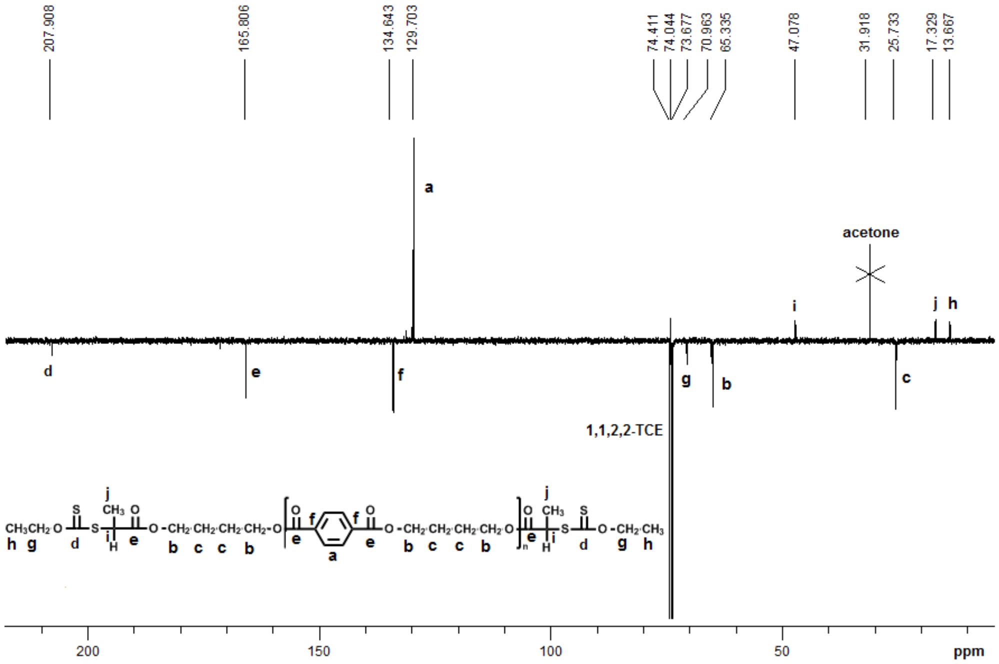

Fig. S3: ^{13}C NMR spectrum of xanthate-end-functionalized PBT synthesized by method B (P2) with peak assignments.

III. MALDI-TOF mass spectrometry

The MALDI-TOF mass spectrum of PBT_B was obtained through the use of a dithranol matrix and trifluoroacetic acid potassium salt as the cationization reagent. Fig. S4 shows the MALDI-TOF spectrum of the xanthate-functionalized PBT_B after the deisotoping procedure. The MALDI-TOF spectrum contains four mass distributions in the range 1000-4000 Da with mass intervals corresponding to the molar mass of the PBT repeating unit (220 u). The most intense distribution at m/z = 442 + 220n + 39 corresponds to the expected PBT chains with xanthate groups at both ends. Species **3b** and **3c** at m/z = 194 + 220n + 39 and m/z = 232 + 220n + 39 are attributed to the potassium adduct of PBT chains bearing the xanthate group at one end and terephthalic acid or COOK functionalities at the other end, respectively. The fourth distribution could be assigned to PBT chains bearing a xanthate functionality at one end and an hydroxyl end-group at the other end.

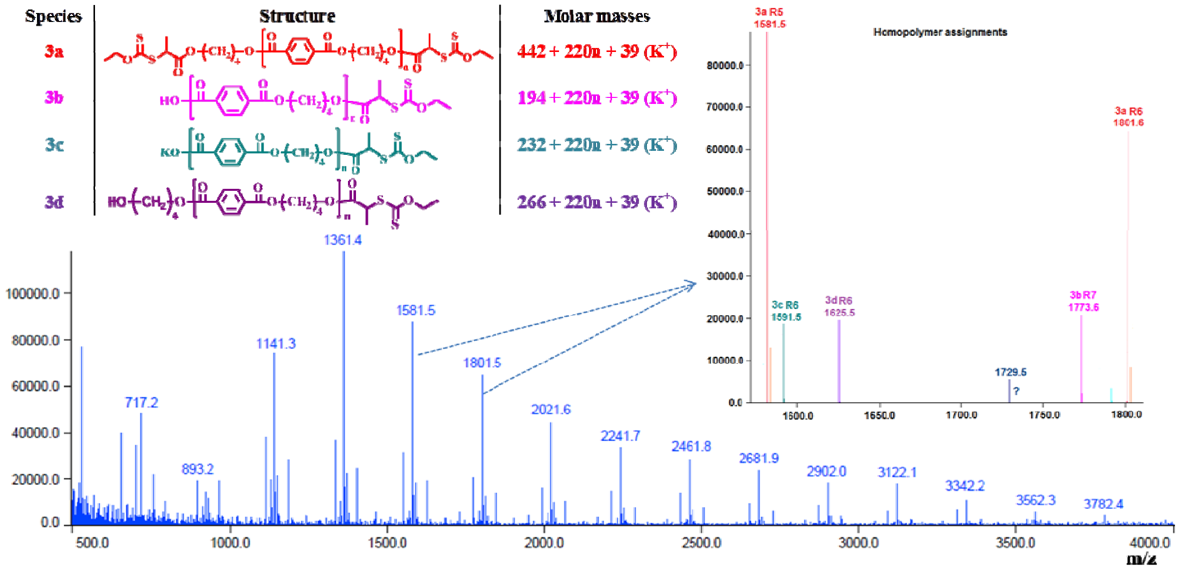

Fig. S4 MALDI-TOF mass spectrum of xanthate end-functionalized PBT synthesized by method B (P2) after deisotoping procedure.

IV. Transfer study to 1,1,2,2-TCE

The procedure for studying transfer to 1,1,2,2 TCE in the RAFT/MADIX polymerization of *n*-BA and *t*-BA was as follows: Rhodixan A1 (supplied by Rhodia) (22 mg), AIBN (5 mg) and acrylate monomer (1 g) were added to an appropriate amount of 1,1,2,2-TCE at 70 °C in a Schlenk tube. Transfer to 1,1,2,2-TCE was studied by varying the amount of solvent in the reaction mixture. The solution was degassed for 15 min by flushing argon. The polymerization was performed at 70 °C keeping a slow stream of argon in the reactor for 4 h. After this period, the solution was characterized by ^{1}H NMR and SEC analyses. It was shown that the experimental molecular weights were very close to the theoretical values. Dispersities were also similar for each experiment. These results have shown that transfer to 1,1,2,2-TCE has no noticeable influence on the control of M_n for P(*n*-BA) and P(*t*-BA) homopolymers.

Table S5 Macromolecular characteristics of the P(*n*-BA) and P(*t*-BA) homopolymers depending of the monomer weight proportion (w_M) in the reaction mixture

Polymer	w_M(%)[a]	Conv[b]	$M_n{}^c{}_{(theory)}$/g mol^{-1}	$M_n{}^d{}_{(SEC)}$/g mol^{-1}	Đ[d]
P(*n*-BA)1	100	0.98	9 650	8 400	1.66
P(*n*-BA)2	70	0.99	9 100	8 900	1.54
P(*n*-BA)3	50	0.99	9 300	9 200	1.73
P(*n*-BA)4	25	0.97	9 350	9 300	1.75
P(*t*-BA) 1	100	0.90	9 050	6 400	1.78
P(*t*-BA) 2	70	0.96	8 000	8 000	1.83
P(*t*-BA) 3	50	0.99	8 350	8 200	1.55
P(*t*-BA) 4	25	0.96	8 100	7 800	1.75

[a] $w_M = m_M/(m_M + m_{Rhodixan} + m_{1,1,2,2\text{-}TCE})$. [b] Conversion determined by ^{1}H NMR ($CDCl_3$). [c] $M_{n\ (theory)}$ = $([M]_0/[Rhodixan]_0)$*conv*MW(M) + $M_{Rhodixan}$. [d] M_n and Đ determined by RI-SEC in THF calibration by PS standards.

V. NMR spectroscopy of P(*n*-BA)-*b*-PBT$_A$-*b*-P(*n*-BA) triblock copolymers

Fig. S6 reports the NMR spectra of two P(*n*-BA)-*b*-PBT$_A$-*b*-P(*n*-BA) copolymers in pure $CDCl_3$ and in a $CDCl_3$:$CHCl_2COOH$ mixture. Experimental molar fraction of PBT (x_{PBT}) was determined by comparing signal **d** characteristic of the two methylene protons next to the ester group in the P(*n*-BA) repeating unit with signal **a** corresponding to four aromatic protons of the PBT repeating unit. By superposing the spectra in both solvents, it was shown that all signals corresponding to the P(*n*-BA) protons (**a**, **b**, **c**, **d**, **e**, **f** and **g**) were superposed, while a partial extinction of the signals **a**, **b** and **c** corresponding to the PBT block was observed in pure $CDCl_3$. This extinction was decreased with an increase of the weight fraction of P(*n*-BA) in the triblock copolymer. The presence of P(*n*-BA) in the copolymer allowed partial solubilization of the PBT block in pure chloroform but is not enough for complete molecular solubilization.

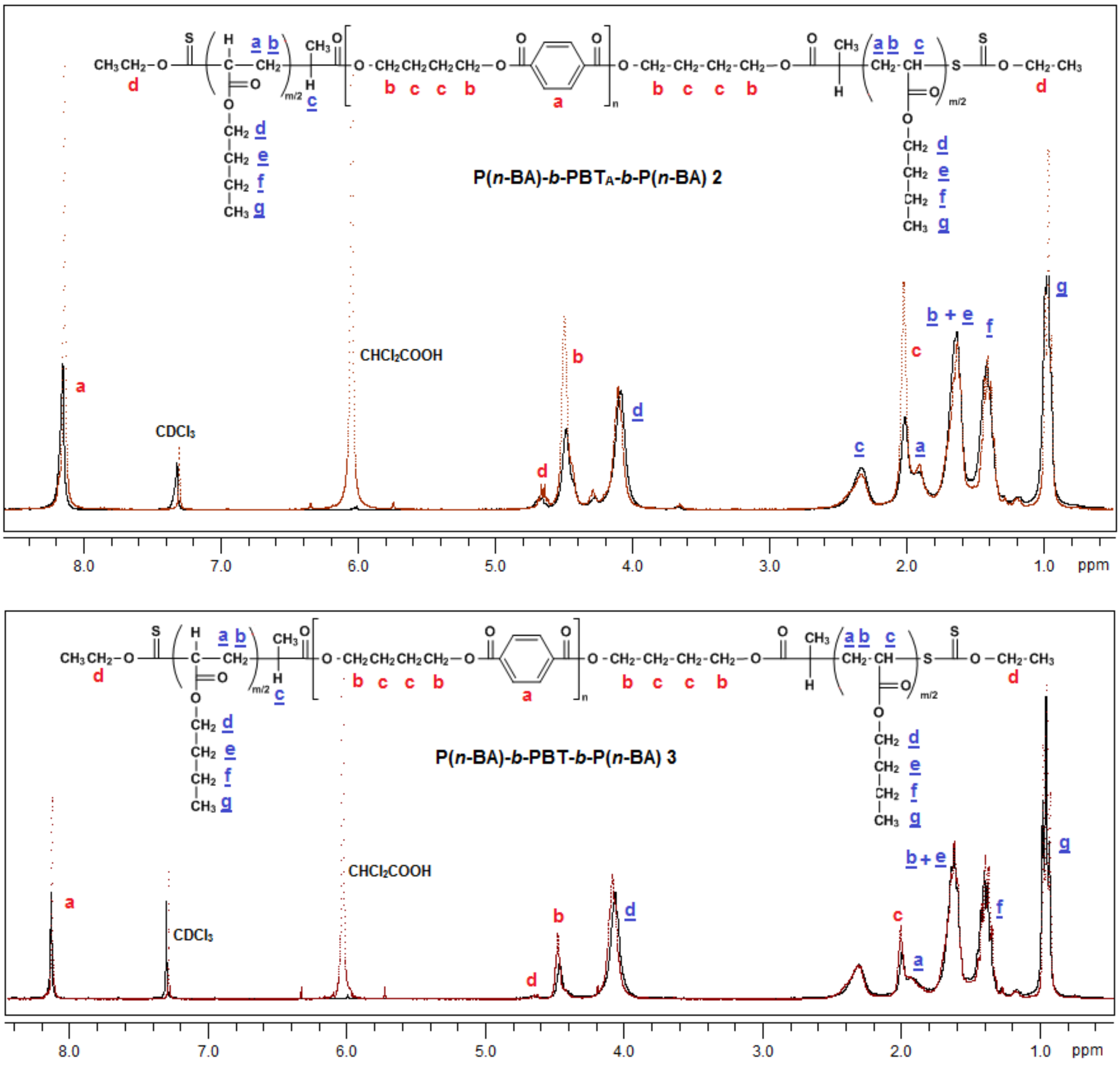

Fig. S6: ^1H NMR spectra of P(*n*-BA)-*b*-PBT-*b*-P(*n*-BA) triblock copolymers in pure $CDCl_3$ (solid line) and in $CDCl_3$:$CHCl_2COOH$ (dotted line).