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Oleksandr Ivanchenko, Maksym Odnoroh, Sonia Mallet-Ladeira, Marc Guerre, Stéphane Mazières, et al.. Azo-Derived Symmetrical Trithiocarbonate for Unprecedented RAFT Control. *Journal of the American Chemical Society*, 2021, 143 (49), pp.20585-20590. 10.1021/jacs.1c10031 . hal-03566047

HAL Id: hal-03566047

<https://hal.science/hal-03566047>

Submitted on 23 Aug 2022

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Azo-derived symmetrical trithiocarbonate for unprecedented RAFT control

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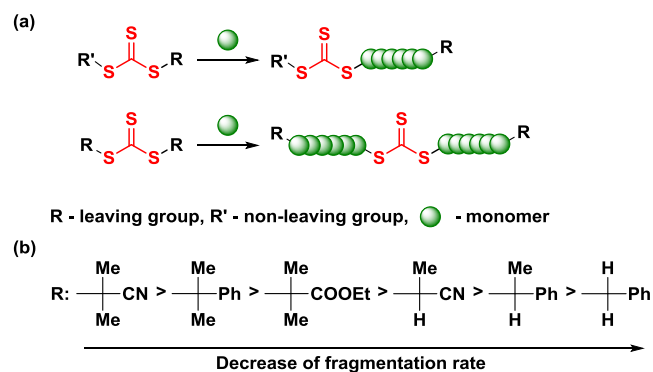
KEYWORDS Trithiocarbonate • Thiol • Polymerization • Block copolymers • Thermoplastic elastomer.

ABSTRACT: Bis(2-cyanopropan-2-yl)trithiocarbonate (**TTC-bCP**) is a new symmetrical trithiocarbonate with the best leaving group ever reported for reversible addition-fragmentation chain transfer (RAFT) polymerization. We propose an elegant route to obtain **TTC-bCP** starting from 2,2'-azobis(2-methylpropionitrile) (AIBN) as a donor of (2-cyanopropan-2-yl) group. **TTC-bCP** allowed the preparation of a high molar mass ($M_n \sim 135 \text{ kg mol}^{-1}$) methyl methacrylate-*n*-butyl acrylate-methyl methacrylate triblock copolymer with unprecedented control ($\mathcal{D} = 1.04$) in reversible-deactivation radical polymerization. Rheology measurements of this triblock copolymer showed a typical thermoplastic elastomer behaviour with a steady rubbery plateau up to 120 °C.

Trithiocarbonates (TTCs) are widely used in medicine,¹ biochemistry,² organic synthesis,³ coordination chemistry⁴ and also in polymer chemistry.^{5,6} In this last domain, TTCs are well-known reversible addition-fragmentation chain transfer (RAFT) agents due to their high efficiency for the controlled polymerization of a large selection of monomers like styrene and derivatives, acrylamides, acrylates and methacrylates.⁶ Many of them are commercially available in small quantities and few of them can be supplied at the industrial scale.^{7,8} Unsymmetrical trithiocarbonates (e.g. $R'=n$ -alkyl, Scheme 1 (a)) control the polymerization of the whole range of the aforementioned monomers provided that the leaving group R is judiciously selected.⁶ In particular for 1,1-disubstituted monomers like methacrylates, only electron-withdrawing and mostly cyano-containing tertiary leaving groups (e.g. 2-cyanopropan-2-yl, Scheme 1 (b)) give satisfactory control of molar mass and dispersity.⁵ On the other hand, symmetrical TTCs (Scheme 1 (a)) possess their own domain of interest, as they are precursors of ABA triblock copolymers following a two-step convergent synthesis procedure.⁵

ABA-type block copolymers with thermodynamically immiscible soft mid-block B (T_g below ambient) and hard amorphous or semi-crystalline A outer blocks can self-organize at the nanometric scale in various morphologies and exhibit thermoplastic elastomer (TPE) properties.⁹ Due to intermolecular physical crosslinks of the rigid domains, TPEs are very attractive materials, which combine the properties of rubber at service temperature with the processability and recyclability of thermoplastics. As a consequence, owing to the increasing demand for more sustainable polymers, triblock copolymers largely contribute to the TPEs market growth¹⁰ with diverse applications

in elastomers, pressure-sensitive adhesives, coatings and toughening agents, to name a few.⁹



Scheme 1. (a) Polymerization of vinyl monomers using either unsymmetrical or symmetrical TTC. (b) Most common leaving groups of RAFT agents

Styrenic block copolymers (e.g. polystyrene-polybutadiene-polystyrene, SBS) are a well-established class of TPEs, which suffer from limited upper service temperatures due to relatively low T_g of the hard domains and limited UV and oxidation resistance caused by their unsaturated nature. All-(meth)acrylic TPEs (i.e. methacrylate-acrylate-methacrylate) present many advantages over styrenic products including optical transparency, weatherability, inherent tack and low viscosity.^{8,11} They were recently developed at the industrial scale by Kuraray using living anionic polymerization¹² and by Arkema via nitroxide-mediated reversible-deactivation radical polymerization (NMP).^{8,13} Even though more constraining from a process standpoint, anionic polymerization yields

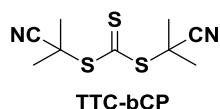
triblock copolymers with better control over macromolecular architecture, especially lower dispersity compared to NMP,¹⁴ atom transfer radical polymerization (ATRP)¹⁵ and RAFT.^{16,17} As a result, the mechanical performances of ABA triblock copolymers derived from reversible-deactivation radical polymerizations (RDRP) still cannot compete with those prepared by living anionic polymerization.^{11,13,15,16} In the quest for all-(meth)acrylic ABA copolymers of low dispersity, RAFT polymerization suffers from a lack of symmetrical TTCs bearing suitable tertiary leaving groups for optimal control of methacrylate polymerization.¹⁷⁻²⁰ As an alternative to symmetrical TTCs with previously reported tertiary leaving groups including carboxy^{17,19,20} and ester¹⁸ functions, we focused our attention on the 2-cyanopropan-2-yl group which is known to provide an optimal fragmentation rate (Scheme 1 (b)).^{6,21}

Synthesis of TTCs can be achieved by several common approaches, such as reaction of potassium trithiocarbonate prepared *in situ* with organic halides.²² This method is mostly suited for primary and secondary R groups. With tertiary halides, nucleophilic substitution is comparatively more difficult with some reports showing no reaction at all,²³ with elimination as a possible side reaction.^{23,24}

Another approach involves the reaction of thiols with thiophosgene²⁵ but due to its toxicity, a safer option is the use of 1,1'-thiocarbonyldiimidazole (TCDI) as a donor of thiocarbonyl group.²⁶ Reaction of TCDI with thiols brings many possibilities to get access to symmetrical TTCs as well as unsymmetrical ones in a one-pot process. However, to our knowledge, this method was never reported with tertiary thiols having an electron withdrawing group, the synthesis of which being potentially challenging.

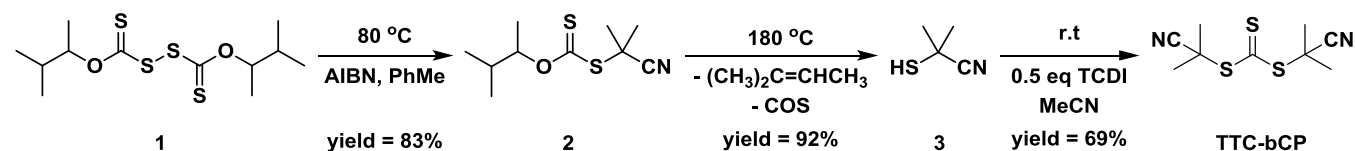
To date, the only reported approach for the preparation of TTCs with a 2-cyanofunctional tertiary R-group was to react a bis(thiocarbonyl) disulfide with a tertiary diazo derivative by free-radical activation.^{27,28}

Only few TTCs were synthesized by this strategy due to limited access to starting disulfides. In addition, symmetrical TTCs with tertiary substituents cannot be synthesized this way.



Scheme 2. Bis(2-cyanopropan-2-yl)trithiocarbonate TTC-bCP

Taking into account all these considerations, we targeted bis(2-cyanopropan-2-yl)trithiocarbonate **TTC-bCP** (Scheme 2) as new promising TTC for the synthesis of



Scheme 3. Synthetic pathway of 2-mercapto-2-methylpropanenitrile 3 and trithiocarbonate TTC-bCP

methacrylate-acrylate-methacrylate triblock copolymers by RAFT polymerization.

Among the aforementioned approaches for the synthesis of TTCs, we selected the reaction of thiols with TCDI. At this stage, access to the corresponding thiol, namely 2-mercapto-2-methylpropanenitrile **3** (Scheme 3), became the crucial step.

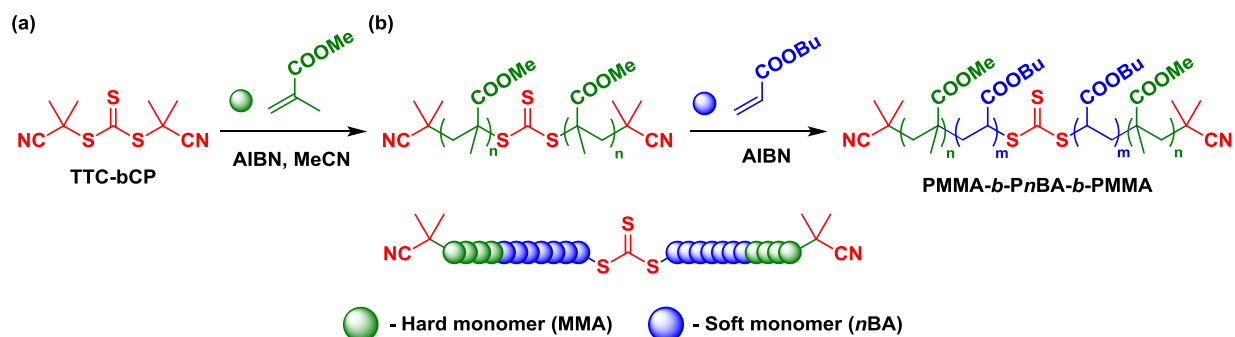
The synthesis of thiol **3** was reported almost 30 years ago,²⁹ but this compound was never used as reactant since then. In their approach, the authors described a complex multi-step synthetic route involving toxic chemicals such as methanol, HgCl₂ and H₂S. Moreover, tedious purification steps were required as thiol **3** was obtained from a water solution and therefore needed to be further dried before its reaction with TCDI, which is a hygroscopic reagent.

In this work, we present a specific and efficient method to synthesize 2-mercapto-2-methylpropanenitrile **3** inspired by the work of Zard³⁰ in which a Chugaev elimination reaction was used to generate a thiol from a xanthate precursor, and by more recent works of our team³¹ where such methodology was applied in the synthesis of thiolactones.

The dithionodisulfide (dixanthogen) **1** (Scheme 3) was synthesized from commercially available 3-methylbutan-2-ol and carbon disulfide using a described method.²⁷ Compound **1** was then reacted with AIBN according to a formerly reported procedure^{27,28} leading to a new xanthate **2**. Thermolysis of xanthates with such O-alkyl group are well known^{27,29-31} and proceed through a Chugaev elimination. In the present synthesis (Scheme 3), after heating xanthate **2** at 180 °C for 90 min, the novel thiol **3** was generated with volatile by-products (COS and 2-methylbut-2-ene) and could be isolated in a pure state without further purification. Its use in the reaction with TCDI constitutes the last step in the synthesis of targeted **TTC-bCP** (Scheme 3).

Conditions reported in the literature³² for the synthesis of TTCs containing electron-withdrawing groups from TCDI, which mainly involved primary and secondary thiols, were unsuccessful with tertiary thiol **3**. In spite of the good nucleophilic character of **3**, typical reaction conditions in toluene at room temperature with KOH as catalyst only led to the corresponding disulfide NC-C(CH₃)₂S-SC(CH₃)₂CN. This product resulting from the direct oxidation of **3** was unexpected considering the good stability of this thiol in air at room temperature. Nonetheless, replacing toluene with a more polar solvent like acetonitrile, in the absence of catalyst, allowed the formation of targeted **TTC-bCP** in relatively good yield (69%).

The product was recrystallized from CHCl₃/*n*-pentane mixture and crystals were analyzed by X-ray diffraction (see section 8 in ESI for details).



Scheme 4. (a) RAFT polymerization of MMA with bis(2-cyanopropan-2-yl)trithiocarbonate TTC-bCP, (b) PMMA-*Pn*BA-PMMA triblock copolymer synthesis

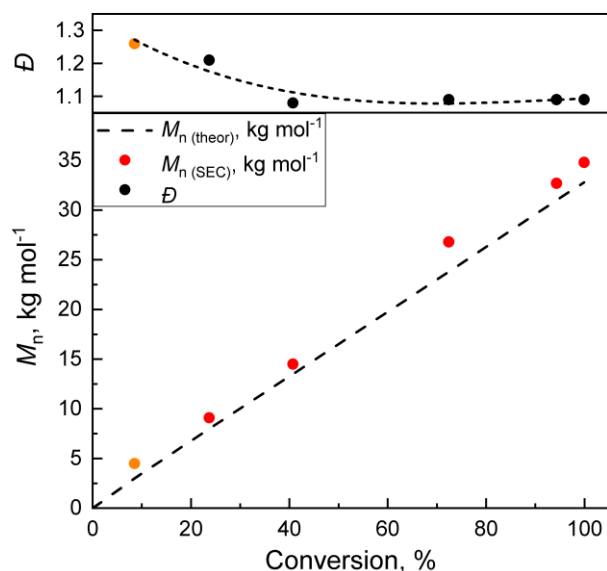


Figure 1. M_n and \bar{D} vs. conversion during PMMA synthesis with **TTC-bCP** at 60 °C in MeCN. Values determined by SEC-RIMALS in THF (except for the lowest conversion data (orange symbol): PMMA calibration).

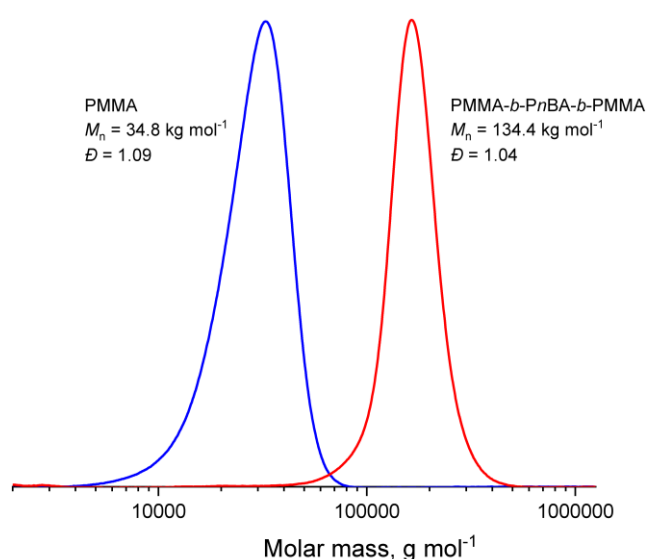


Figure 2. SEC traces of PMMA-**TTC-bCP** and PMMA-*Pn*BA-PMMA triblock copolymer

TTC-bCP was first evaluated for the RAFT polymerization of MMA at 60 °C in acetonitrile with AIBN initiator (Scheme 4 (a)). From Fig. 1, it appears that controlled polymerization ($\bar{D} < 1.26$) and low dispersities ($\bar{D} < 1.26$) are obtained from the early stages of polymerization (24% MMA conversion), which arises from the fast addition-fragmentation of **TTC-bCP**. At higher conversions, M_n increases linearly with MMA conversion in agreement with theoretical expectations, and \bar{D} values decrease and stabilize to 1.08-1.09 between 40.7 and 99.9% conversion (Table S1, entries 1-6). Size exclusion chromatography (SEC) equipped with refractometric (RI) and UV detectors confirmed that chromatograms are monomodal and reveal the presence of TTC mid-chain fragment because of its strong UV absorbance ($\lambda = 290$ nm) (Fig. S13a-b). Also, ESI-MS analysis of a low molar mass PMMA confirmed the incorporation of **TTC-bCP** in the polymer with PMMA-**TTC-bCP** as the only observed population (see section 6 in ESI for details). Due to the comparatively faster fragmentation of its 2-cyanopropan-2-yl group, **TTC-bCP** is a much better RAFT agent for MMA than any other symmetrical TTCs of the literature.¹⁷⁻²⁰ As a basis for comparison, *S,S'*-bis(α,α' -dimethylacetic ac-

id)trithiocarbonate (BDAT), which is the most frequently reported symmetrical TTC for RAFT polymerization of methacrylates,^{17,19,20} is only moderately reactive and responsible for uncontrolled M_n throughout polymerization and relatively high dispersities (\mathcal{D} in the 1.4-1.7 range for MMA^{19,20} and 1.5-1.8 for terpene methacrylates).¹⁷

Using **TTC-bCP** for the polymerization of *n*-butyl acrylate (*n*BA) in toluene at 60 °C (Table S1, entries 7-11 and Fig. S14 a-b), we observed an excellent control over M_n with low dispersities ($\mathcal{D} = 1.05$ -1.10) throughout polymerization. For the *n*BA polymerization step in triblock copolymer synthesis of higher molar mass, bulk conditions were preferred in order to avoid any contribution of chain transfer to solvent.

An ABA block copolymer was prepared (Scheme 4b) with PMMA as a hard block A and *Pn*BA as a soft block B. The SEC chromatogram of Fig. 2 showed a successful chain extension of PMMA-**TTC-bCP** during *n*BA polymerization at 60 °C, yielding a PMMA-*Pn*BA-PMMA triblock copolymer free of residual PMMA macro-CTA, with a controlled M_n of 134.4 kg mol⁻¹ and a remarkably low \mathcal{D} of 1.04 (Table S1, entry 12).

Here again, intense SEC-UV traces of both PMMA macro-chain transfer agent and final triblock copolymer reflect the very high proportion of chains bearing the TTC fragment (Fig. S15).

Differential scanning calorimetry (DSC) measurements gave glass transition temperatures (T_g) close to the T_g of the corresponding homopolymers (-57 °C and 124 °C for the soft and hard blocks respectively), which indicated phase separation of the constituting blocks (Fig. S17). The increase of the T_g of the PMMA block to 124 °C (instead of 100 °C for pure PMMA) was previously reported for some nanophase-separated, acrylic block copolymers of MMA.³³

The phase separation was further verified through rheology measurements. Fig 3. displays the temperature dependence of G' and $\tan \delta$ of PMMA_{17.4K}-*Pn*BA_{99.6K}-PMMA_{17.4K} triblock copolymer. The material behaved as an elastomer in temperature up to 110-120 °C with a storage modulus of 0.25 MPa at 50 °C. The progressive drop of G' in this range of temperature in combination with a sudden increase of $\tan \delta$ is a characteristic signature of the melt flowing of TPEs. This transition corresponds to the loss of network integrity as a result of the hard phase collapsing. Nonetheless, the drop is very progressive suggesting a non-Newtonian behaviour even at temperatures 60 °C above T_g . This behaviour was already reported by Tong et al.³⁴ in similar PMMA-based triblock copolymers and was attributed to persisting PMMA domains. The T_g value obtained by rheology measurements is in good agreement with the one determined by DSC and confirms the tendency of PMMA blocks to exhibit higher T_g in acrylic block copolymers.

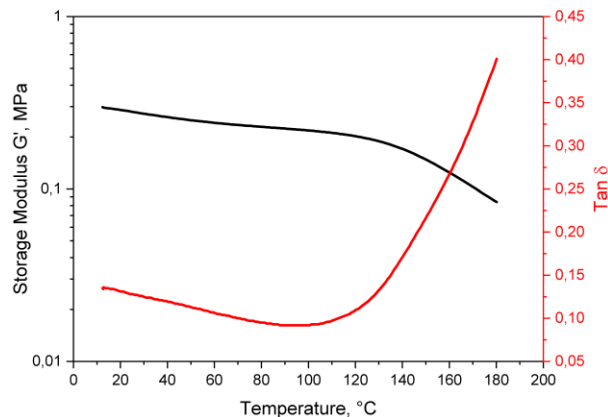


Figure 3. Temperature dependence of G' and $\tan \delta$ of PMMA-*Pn*BA-PMMA triblock copolymer (Table S1, entry 12)

In conclusion, we report the synthesis of the long-awaited symmetrical trithiocarbonate derived from AIBN (**TTC-bCP**) following an original methodology. For the first time, a low dispersity ($\mathcal{D} < 1.1$) PMMA-*Pn*BA-PMMA triblock copolymer of relatively high M_n (~135 kg mol⁻¹) was synthesized by a convergent RAFT process in two steps. The material exhibits dispersities comparable to counterparts derived from living anionic polymerization.^{12,15} Phase separation of the constitutive blocks with typical thermoplastic elastomer behaviour was observed. This work opens many perspectives for trithiocarbonate RAFT agent design considering the broad range of commercially available diazo initiators. In addition, **TTC-bCP** offers a rich toolbox for ABA copolymer synthesis with great variability of molar mass, composition and monomer selection (an increasing number of (meth)acrylates being partly biosourced)³⁵ to finely tune thermomechanical properties towards applications as more sustainable TPEs. This will be the subject of forthcoming studies.

ASSOCIATED CONTENT

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/xxxx>.

It includes experimental procedures for all reactions and characterization data for all products, including crystallographic data and UV-Vis spectroscopy analysis of **TTC-bCP**, and ESI-MS, DSC and additional SEC analyses of (co)polymers (PDF).

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Author Contributions

The manuscript was written through contributions of all authors.

Funding Sources

Authors thank the French Ministry of Higher Education, Research and Innovation for financial support of O.I.

ACKNOWLEDGMENT

The authors thank Valérie Bourdon and Pascale Laborie, Institut de Chimie de Toulouse ICT-UAR 2599, for their valuable help with ESI-MS and SEC analyses, respectively. Dr Andrii Karpus is acknowledged for fruitful discussions.

ABBREVIATIONS

TTC, trithiocarbonate; RAFT, reversible addition-fragmentation chain transfer; NMP, nitroxide-mediated reversible-deactivation radical polymerization; TPE, thermoplastic elastomer; SEC, size exclusion chromatography; DSC, differential scanning calorimetry; ATRP, atom transfer radical polymerization; TCDI, 1,1'-thiocarbonyldiimidazole; MMA, methyl methacrylate; nBA, n-Butyl acrylate; AIBN, 2,2'-azobis(2-methylproprionitrile)

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