

Thermal stability of RAFT-based poly(methyl methacrylate): A kinetic study of the dithiobenzoate and trithiocarbonate end-group effect

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ABSTRACT

Thermal stability of dithiobenzoate- (DB) and trithiocarbonate- (TC) terminated poly(methyl methacrylate) (PMMA) synthesized via reversible addition–fragmentation chain transfer (RAFT) polymerization is systematically studied under dynamic heating and prolonged isothermal treatment at 100–180 °C. It is demonstrated that in the presence of functional end-groups the onset of mass loss can be shifted relative to conventional PMMA, either toward higher (PMMA-DB) or lower (PMMA-TC) temperatures. Irrespective of the polymer molar mass, a loss of PMMA chain-end functionality clearly manifests itself upon 24 h of isothermal treatment at 120 °C for DB end-groups and already at 100 °C for TC ones. At 120 °C (for PMMA-TC) and 140 °C (for PMMA-DB) the ability of both polymers to serve as macromolecular RAFT agents in the chain extension processes ceases almost completely. The kinetics of functional end-groups elimination depends on their chemical nature. In the case of DB-groups, the reaction is of the first order, whereas TC-groups containing two C–S bonds demonstrate more complex degradation kinetics. We propose a two-step mechanism of TC-group elimination, which enables interpretation of the observed experimental data.

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1. Introduction

Radical addition–fragmentation chain transfer (RAFT) polymerization remains one of the most attractive and versatile polymerization techniques for the controlled synthesis of macromolecules of complex architecture, even after two decades since its discovery [1–20]. According to the RAFT mechanism, α - and ω -groups of macromolecules grown in the presence of a thiocarbonylthio compound are R– and –S–C(=S)–Z fragments derived from an initial R–S–C(=S)–Z RAFT agent [1,7,8]. Such terminal groups can be formed under the following conditions: 1) a RAFT agent is effective in the polymerization of chosen monomers, being rapidly consumed at low conversions; 2) most of the chains are formed due to the RAFT agent, whereas the amount of chains

derived from an initiator is negligible, which means that [RAFT agent]/[initiator] \gg 1; 3) side reactions due to the intermediate radical termination play minor role in the polymerization. All of these can be easily attained by choosing an appropriate RAFT agent and polymerization conditions.

The application fields of RAFT-synthesized polymers are determined by a set of factors including the chemical nature of repeating units and terminal groups, chain microstructure and topology. Thermal stability seems to be one of the important issues for their application in bulk. The first studies using TGA at a heating rate of 5–10 °C/min have not revealed essential distinctions in the thermal stability of polymers synthesized with and without RAFT agents [21–26]. For instance, the thermal degradation of both types of poly(butyl acrylate) (PBA) starts at similar temperatures [21,22]. Later it was demonstrated that the prolonged heating of PBA above 180 °C and polystyrene (PS) above 200 °C in inert atmosphere results in the cleavage of thiocarbonylthio groups [26,27]. This reaction takes place at lower temperatures than the thermal degradation recorded by TGA. In the case of PS, PBA, or their copolymers bearing trithiocarbonate groups in the backbone, it results

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not only in a loss of thiocarbonylthio functionality but also in a noticeable decrease in the molar mass of the polymers [28–30]. In general, the thermal stability of RAFT-based polymers decreases among poly(vinyl acetate) > poly(N-vinyl pyrrolidone) > PBA > PS > poly(N-isopropylacrylamide) > poly(methyl methacrylate) (PMMA) and among the Z-groups as dithiobenzoate > trithiocarbonate > xanthate > dithiocarbamate [21–35]. For low molar mass RAFT agents, it is typically lower compared to that of RAFT-synthesized polymers, however, the recent study by Zhou et al. doubts this statement [34].

Chemical nature of the Z-group of an initial RAFT agent determines the kinetics of the thermal degradation of RAFT-synthesized polymers. Surprisingly, the literature reveals some discrepancy regarding RAFT-based PMMA. According to the TGA data, PMMA with a methyl trithiocarbonate group undergoes three stages of mass loss with the first step starting at 170 °C, whereas the thermal degradation of PMMA with a terminal dithiobenzoate group proceeds in one stage above 200 °C [27]. A three-stage degradation process was reported by Roy et al. for PMMA with a dodecyl trithiocarbonate end-group, with the first step starting at ca. 160 °C and the activation energy being about 185 kJ/mol [36]. A similar three-stage degradation process starting at 120–130 °C was detected by Lima et al. for dithiobenzoate-terminated PMMA [22]. At the same time, PMMA synthesized with a “switchable” 2-cyanopropan-2-yl N-methyl-N-(pyridine-4-yl)-carbamodithioate undergoes the first step of mass loss at 110–135 °C in the protonated form of the Z-group and at 120–150 °C in its neutral form [31]. In general, depending on the nature of the Z-group, RAFT-based PMMA can be either more or less stable than PMMA synthesized in the absence of RAFT agent, which typically degrades above 200 °C.

The study of this process under isothermal conditions has not made the situation any clearer. The ¹H NMR analysis of PMMA ($M_n = (10–50) \times 10^3$ g/mol) end-groups heated at 5 °C/min from 50 °C to a desired temperature within the 140–240 °C range and then isothermally annealed for 20 min revealed a complete conversion of dithiobenzoate and methyl trithiocarbonate end-groups at 180 °C. The cleavage rate for the both types of thiocarbonylthio groups was comparable [27]. Oligomeric PMMA with $M_n \sim 3600$ g/mol synthesized with cumyl dithiobenzoate was found to start losing its thiocarbonylthio functionality after 1 h of heating in a *tert*-butyl benzene solution at 120 °C and its decomposition rate depended on the initial PMMA concentration [32], contrary to the data of ref. 27. At the same time, chain extension of PMMA pre-heated at 120 °C confirmed the living nature of polymerization. Moreover, the thermal stability of PMMA with and without dithiobenzoate groups was equal. This illusory contradiction may come from the contamination of pre-heated PMMA with dithiobenzoic acid that can attach to double C=C bond with *in situ* formation of dithiobenzoate thus promoting RAFT polymerization [3]. Similar results on the thermal stability of dithiobenzoate-terminated PMMA were later obtained for the polymer with close MM ($M_n \sim 2800$ g/mol) in a *tert*-butyl benzene solution [34]. The authors of ref. 34 have applied numerous techniques to study a wide variety of RAFT/MADIX agents in the temperature range from 100 to 160 °C and reported that the dithiobenzoate group cleavage in PMMA takes place at a rate of $4.05 \times 10^{-5} \text{ s}^{-1}$ at 120 °C with the activation energy of 77.6 kJ/mol.

It is reasonable to suppose that the use of different experimental techniques and experimental conditions underlies the apparent contradictions mentioned above. That is why the accuracy of the kinetic data on the thermal degradation of RAFT-based PMMA remains in question, in contrast to the mechanism of thiocarbonylthio group cleavage.

Evidently, the mechanism of thermolysis of RAFT-synthesized polymers depends on the chemical nature of a polymeric

substituent and Z-group. For example, PBA with butyl trithiocarbonate group undergoes C–S bond homolysis, backbiting, and β -scission, which result in the formation of a macromonomer with an exo-methylene double bond [21,27]. Thermolysis of PS containing the same terminal group proceeds via Chugaev's elimination mechanism [37], being accompanied by the elimination of a butyl trithiocarbonate group and the formation of a PS macromonomer [26]. In the case of a xanthate-terminated PS, a polymer with a thiol-end group is formed [26].

For RAFT-based PMMA, the mechanism of thermolysis is also determined by the nature of the Z-group. In the case of trithiocarbonate and dithiobenzoate terminal groups, the macromonomers are formed [26,27,33] via elimination (a) and disproportionation (b), as shown in Scheme 1. A more complicated situation is observed for a “switchable” dithiocarbamate [31], in which case the multistage thermal degradation does not result in a macromonomer formation.

Thus, the thermal stability of RAFT-synthesized PMMA under prolonged heating and its degradation kinetics remain debatable. Aiming to address this problem, we analyze the thermal behavior of PMMA of various MM with dithiobenzoate and trithiocarbonate end-groups in the temperature range of 100–180 °C under the isothermal conditions in vacuum, as well as the kinetics of thiocarbonylthio group cleavage at a chosen temperature. The polymer MMD before and after thermal treatment, the molar fraction of thiocarbonylthio groups, and the ability of pre-heated polymers to promote chain extension are systematically studied.

2. Experimental

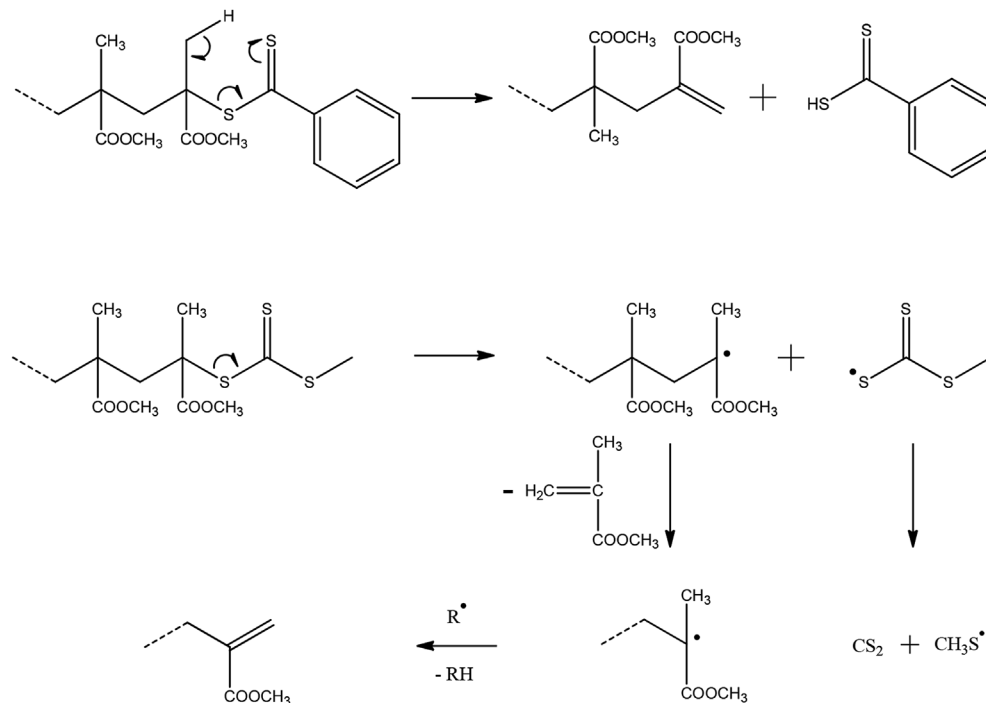
2.1. Materials and polymer synthesis

Methyl methacrylate (Aldrich) was distilled under reduced pressure before use. RAFT agents, 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (CPTPA) and S-(2-cyano-2-propyl)–S-dodecyl trithiocarbonate (CPDTC), were purchased from Aldrich and used as received. Azobisisobutyronitrile (AIBN) initiator (Aldrich) was recrystallized twice from methanol before use. Solvents, benzene, DMF, and THF (Chimmed, Russia), were distilled before use. Acetone (Chimmed, Russia) and methanol (Aldrich) were used without purification.

To synthesize PMMA, the required amounts of AIBN and, if necessary, of RAFT agent were dissolved in MMA. Then the solution was poured into an ampoule, degassed by repeating three freeze – evacuate – thaw cycles and sealed under vacuum. After keeping for 24–48 h at 80 °C the reaction mixture was cooled, then the polymer was dissolved in benzene and precipitated in methanol. Table 1 summarizes the experimental conditions of the synthesis, as well as molar mass characteristics of the synthesized PMMA.

For isothermal thermolysis, the polymer (0.1 g) was placed into an ampoule. After degassing and sealing, the ampoule was put into an oven at a desired temperature (100, 120, 140, 160, and 180 °C; ± 1 °C) for 24 h. After preliminary studies, the kinetics of the thiocarbonylthio group cleavage was investigated. The PMMA samples with dithiobenzoate end-group (PMMA-DB1 – PMMA-DB3) and trithiocarbonate end-group (PMMA-TC1 – PMMA-TC3) were kept at the chosen temperature for a given time and then cooled down by placing them in liquid nitrogen. The polymers were dissolved in acetone, precipitated in methanol, centrifuged, separated from methanol, triple washed with methanol until decoloration of the methanol solution, and then dried in vacuum before SEC and UV–vis spectroscopy characterization. The absence of dithiocarbonyl chromophore in the mother liquor collected after the last washing with methanol was confirmed by UV–vis spectroscopy.

To verify the ability of PMMA to serve as a polymeric RAFT agent



Scheme 1. Thermolysis of PMMA with dithiobenzoate (a) and trithiocarbonate (b) terminal groups [26].

Table 1
Conditions of the synthesis and molar mass characteristics of PMMA.^a

Polymer	[RAFT agent], mol/L	[AIBN], mol/L	Conversion, %	M_n , g/mol (theory ^e)	M_n , g/mol (SEC)	M_n , g/mol (UV ^f)	$\bar{D} = M_w/M_n$
PMMA-DB1 ^b	CPTPA, 3.2×10^{-2}	1×10^{-4}	33.4	9400	9600	10000	1.11
PMMA-DB2	CPTPA, 3.2×10^{-2}	5×10^{-4}	50.2	13900	14000	13300	1.08
PMMA-DB3	CPTPA, 1×10^{-2}	1×10^{-4}	32.0	28100	29800	28400	1.16
PMMA-TC1 ^c	CPDTC, 6.5×10^{-2}	1×10^{-3}	55.1	7700	7700	8000	1.23
PMMA-TC2	CPDTC, 3×10^{-2}	5×10^{-4}	50.0	14800	14900	14200	1.25
PMMA-TC3	CPDTC, 1×10^{-2}	1×10^{-4}	38.0	33400	33600	35200	1.22
PMMA ^d	—	1×10^{-3}	91.1	—	17100	—	1.93

^a Polymerization was conducted in bulk at 80 °C.

^b DB denotes dithiobenzoate end-group.

^c TC denotes trithiocarbonate end-group.

^d Synthesized via conventional radical polymerization in benzene solution, [MMA] = 2.5 mol/L.

^e Theoretical values of M_n are calculated as $M_n = \text{conv.}[MMA]_0/[\text{RAFT agent}]_0$.

^f M_n values are calculated basing on the assumption of one dithiocarbonylthio group per chain.

after prolonged isothermal treatment, the chain extension experiments were carried out. To this end, the polymer (0.07 g) subjected to the isothermal thermolysis was added to MMA containing 10^{-3} mol/L of AIBN. The prepared solution was poured into an ampoule, degassed by repeating three freeze – evacuate – thaw cycles, and sealed. The polymerization was conducted for 24 h at 80 °C. After that, the polymer was dissolved in acetone, precipitated in methanol, centrifuged, dried in vacuum, and then analyzed by SEC.

2.2. Instrumentation

The average molar mass and dispersity (\bar{D}) were characterized by size exclusion chromatography (SEC). The measurements were performed in DMF containing 0.1 wt % of LiBr at 50 °C with a flow rate of 1.0 mL/min using a chromatograph GPC-120 “PolymerLabs” equipped with a refractive index detector and two PLgel 5 μ m MIXED B columns for the MM range from 5×10^2 to 1×10^7 g/mol. The SEC system was calibrated using narrow-dispersed linear PMMA standards with MM ranging from 800 to 2×10^6 g/mol. A second-order polynomial was used to fit the dependence of $\log_{10}M$

on retention time.

The concentration of thiocarbonylthio end-groups in PMMA was measured in THF on a Unico 2804 UV–vis spectrometer (USA) using the molar extinction ratio of CPTPA in THF equal to $(16.0 \pm 0.3) \times 10^3$ mol/(L \times cm) for PMMA-DB and the molar extinction ratio of CPDTC in THF equal to $(10.2 \pm 0.9) \times 10^3$ mol/(L \times cm) for PMMA-TC (Fig. S1, Supplementary data).

Thermogravimetric analysis (TGA) was carried out with a synchronous thermal analyzer STA 449 F3 Jupiter (Netzsch). The mass loss of a 15–20 mg PMMA sample placed in a corundum crucible was analyzed in the linear heating mode (10 °C/min from 25 to 450 °C) under argon flow of 50 mL/min.

3. Results and discussion

3.1. Dynamic thermolysis

Thermal degradation of PMMA occurs via depolymerization mechanism, i.e. its chains depropagate to monomers [38–42]. However, the primary step of degradation depends on the nature of

weak bonds in the macromolecules. TGA analysis reveals that PMMA synthesized via conventional free radical polymerization may undergo two or three steps of mass loss due to the cleavage of head-to-head and head-to-tail (vinyl terminated PMMA) linkages and random scission (saturated PMMA) [38–41]. Degradation of PMMA synthesized via anionic polymerization is also initiated via random scission [42]. PMMA synthesized via reversible deactivation radical polymerization (ATRP or RAFT) reveals typically higher thermal stability that radically synthesized PMMA [43,44].

Fig. 1 presents TGA thermograms of PMMA samples with close molar masses (MM) obtained by RAFT (curves 1, 2) and via conventional radical polymerization (curve 3) under argon atmosphere. As is seen, PMMA terminated with dithiobenzoate group is more stable than radically synthesized PMMA that contains more weak bonds. In contrast, PMMA terminated with a dodecyl tri-thiocarbonate group starts to degrade at a lower temperature. However, the main degradation process of PMMA-DB and PMMA-TC occurs in the same temperature range above 300 °C. The qualitative and quantitative similarity of PMMA-DB2 ($M_n = 14000$ g/mol, Table 1) and PMMA-TC2 ($M_n = 14900$ g/mol, Table 1) thermograms with the data discussed in ref. 27 leads to the conclusion that the thermal stability of RAFT-based PMMA is independent of the polymer MM at least for PMMA with M_n above 10^4 g/mol. It agrees with the conclusion made in ref. 27. Though other studies [39,42] emphasized the role of free radicals, which are able to considerably accelerate the degradation rate and even qualitatively change the apparent kinetics, this factor seems to be under control in our experiments.

One can see that the first step of mass loss in PMMA-DB2 occurs in the temperature range 120–200 °C and results in a mass change of 2.1 wt% which corresponds to the splitting off of dithiobenzoic acid [27]. It differs from the data given in ref. 43 that reports 8 wt% loss in PMMA-DB of larger MM ($M_n = 32500$ g/mol) in the same temperature range. We suppose that the residual impurities, e.g. initiator, or head-to-head linkage may cause formation of radicals and additional initiation of chain destruction. A noticeable mass loss in PMMA-DB2 starts at about 300 °C (curve 1) and coincides with the last step of mass loss in “conventional” PMMA (curve 3). The major loss (95.8 wt%) in PMMA-DB2 may be predominantly due to β -scission of weak C–C bond β to terminal vinyl group, which is formed after the splitting off of dithiobenzoic acid, and it continues by depropagation to monomer. The analysis of the literature data [38–42] allows us to conclude that not only weak bonds but polymer purity and age as well determine thermal stability of PMMA.

In contrast, the thermal stability of PMMA-TC2 is much lower (curve 2). The first step of mass loss in PMMA-TC2 occurs in the temperature range of 100–170 °C and results in a mass change of

1.6 wt%. A mass loss of about 19% is observed in the temperature range of 170–250 °C. Other steps of mass loss are similar to those in PMMA-DB2. We can suppose that the unusual behavior of PMMA-TC thermal degradation is due to the presence of two weak C–S bonds in its structure. We will return to this issue after studying the process kinetics.

The effect of thiocarbonylthio moiety removal on the thermal degradation of PMMA is illustrated in Fig. 1b. Preliminarily, PMMA-DB1 with $M_n = 9600$ g/mol was subjected to the thermal treatment in vacuum for 24 h at 140 °C. Then it was purified by reprecipitation to remove dithiobenzoic acid and analyzed by SEC, UV-spectroscopy, and TGA. The SEC analysis confirmed that the molar mass distribution was not changed and the UV-spectra confirmed the removal of dithiobenzoic acid. According to the synthesis conditions, the major part of chains in pristine PMMA-DB1 are living (Table 1). After thermal treatment, they should contain unsaturated (vinyl) terminal groups due to the splitting off of dithiobenzoic acid, while the minor part of chains may contain head-to-head linkages and saturated terminal groups derived from initially dead chains. Nevertheless, as seen from Fig. 1b, the thermal stability of PMMA-DB1 before and after the thermal treatment is comparable and the major loss in the treated PMMA-DB1 still starts above 300 °C, in agreement with the data of ref. 43. Thus, we can conclude that the cleavage of DB moieties under controlled conditions does not produce free radicals that can facilitate degradation of remaining macromolecules.

3.2. Isothermal thermolysis

3.2.1. Poly(methyl methacrylate) with dithiobenzoate end-group

PMMA-DB1 ($M_n = 9600$) was subjected to the thermal treatment in vacuum for 24 h at 100, 120, 140, 160, and 180 °C. Then the samples were carefully purified from low molar mass products and analyzed by SEC and UV–vis spectroscopy. UV–vis spectroscopy is a simple and robust technique which allows quantitative evaluation of the molar concentration of dithiocarbonyl chromophore [26–30]. As is seen from Fig. 2 and Table 2, the thermolysis does not affect the polymer MMD, which is consistent with the data by Chong et al. [27] Depending on the temperature (Fig. S2), the heated samples varied in color from pink (100 °C) to daffodil (180 °C). Decoloration of the polymer is attributed to the cleavage of dithiobenzoate chromophore [45].

To quantitatively estimate the amount of “living” chains, i.e., the chains that kept their dithiobenzoate functionality, we applied UV–vis spectroscopy based on the molar extinction ratio of a dithiobenzoate group [46]. Fig. 3a illustrates the absorption spectra of the initial PMMA-DB1 and CPTPA used for the polymer synthesis, both dissolved in THF in the same concentration. As is seen from the

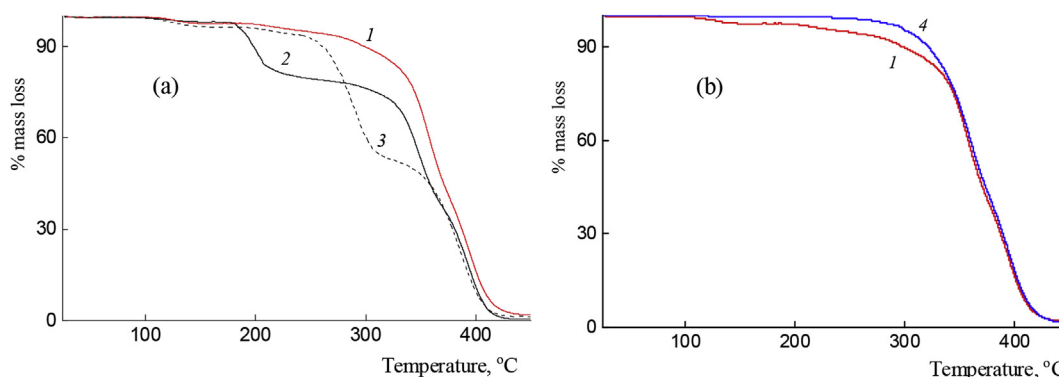


Fig. 1. Percentage mass loss in PMMA-DB2 (1), PMMA-TC2 (2), PMMA (3) with MMD characteristics given in Table 1 and PMMA-DB1 (4) after thermal treatment for 24 h at 140 °C.

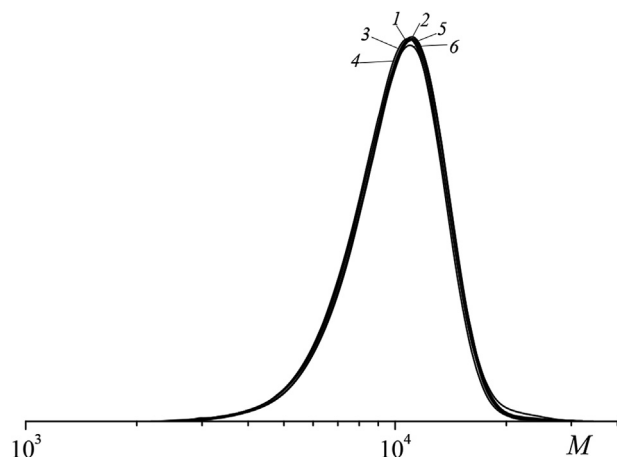


Fig. 2. SEC traces of PMMA-DB1 before (1) and after the thermal treatment in inert atmosphere during 24 h at 100 (2), 120 (3), 140 (4), 160 (5), and 180 °C (6) normalized to the unit area.

UV–vis spectra, an intense maximum at 300–306 nm and a low intense maximum at 509–513 nm are observed for both low molar mass and polymeric RAFT agents. Fig. 3b presents the UV–vis spectra of PMMA-DB1 before (1) and after (2–6) its thermal treatment at different temperatures and at a constant molar concentration of the polymer. The absorbance maximum intensity at 306 nm decreases with the thermolysis temperature in the range of 100–120 °C and vanishes at 140 °C and above.

The molar concentration of dithiobenzoate groups in the polymer derived from the UV–vis data and molar fraction of “living” chains are given in Table 2. One can notice that the concentration of dithiobenzoate end-groups in PMMA after 24 h of thermolysis at 140 °C and above tends to zero. On the one hand, these results do not contradict the data reported by Chong et al. [27], since we used much (72 times) longer thermal treatment. On the other hand, the thermal stability of dithiobenzoate-terminated PMMA is higher than reported by Xu et al. [32]. Thus, the PMMA-DB1 samples subjected to a prolonged thermal stress at 140 °C and higher temperatures should lose their ability to promote chain extension as polymeric RAFT agents.

To verify the above conclusion, chain extension experiments with PMMA-DB1 pre-heated at various temperatures were conducted. After purification from low molar mass compounds, the polymer samples were used for MMA polymerization initiated by 10^{-3} mol/L AIBN and carried out at 80 °C for 24 h. In all the experiments the concentration of macromolecules was kept constant at 10^{-3} mol/L. The results are presented in Fig. 4.

It is seen that at the monomer conversion of 85–92% the

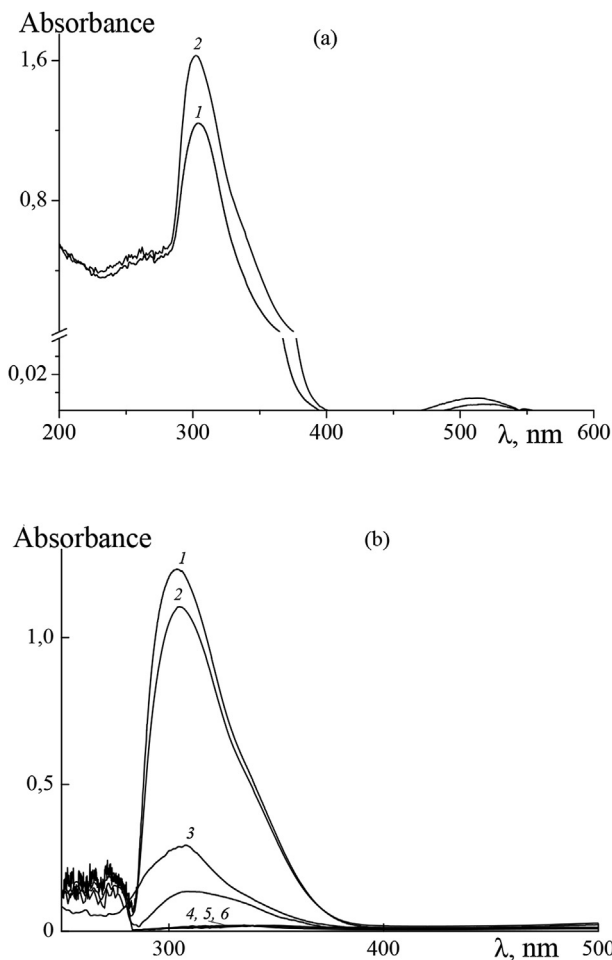


Fig. 3. UV–vis spectra of (a) CPTA (1) and PMMA-DB1 (2) in THF at 25 °C and of (b) PMMA-DB1 before (1) and after the thermal treatment in inert atmosphere during 24 h at 100 (2), 120 (3), 140 (4), 160 (5), and 180 °C (6).

polymer MMD depends on the temperature of thermal stress. The products of chain extension with the initial PMMA-DB1 (curve 1) and PMMA after thermolysis at 100 °C (curve 2) are characterized by narrow MMDs and close values of the average molar masses thus independently confirming the UV–vis data. The molar fraction of dithiobenzoate groups decreases after storing the sample at 120 °C. Under the $[AIBN]/[“living”\ chains] > 1$ condition, it results in the broadening of the main MMD peak (curve 3). The whole distribution is bimodal due to the presence of the PMMA-DB1 fraction with lost dithiobenzoate functionality. A noticeable increase in the

Table 2

Characteristics of PMMA-DB1 subjected to the thermal treatment for 24 h and then used for chain extension.

T, °C	M_n , g/mol	\bar{D}	[PhC(=S)S], mol/L ^a	Molar part of “living” chains % ^a	Chain extension ^b	
					$M_n \times 10^{-3}$, g/mol	\bar{D}
—	9600	1.11	0.75×10^{-4}	~100	170 ^c	1.21
100	9500	1.10	0.71×10^{-4}	92	180	1.21
120	9600	1.10	0.14×10^{-4}	19	210	1.81
140	9600	1.09	1.0×10^{-6}	<1.0	370	2.2
160	9600	1.09	0.5×10^{-6}	<1.0	230	2.5
180	9500	1.09	0.5×10^{-6}	<1.0	280	2.5

^a Determined by UV–vis spectrometry in THF using the same mass concentration of the polymer. Molar fraction of living chains was calculated as the ratio of the current concentration of dithiobenzoate chromophore to the total polymer concentration.

^b Chain extension was conducted at 80 °C for 24 h using $[PMMA] = [AIBN] = 10^{-3}$ mol/L.

^c Theoretical value of M_n is 174 000 g/mol.

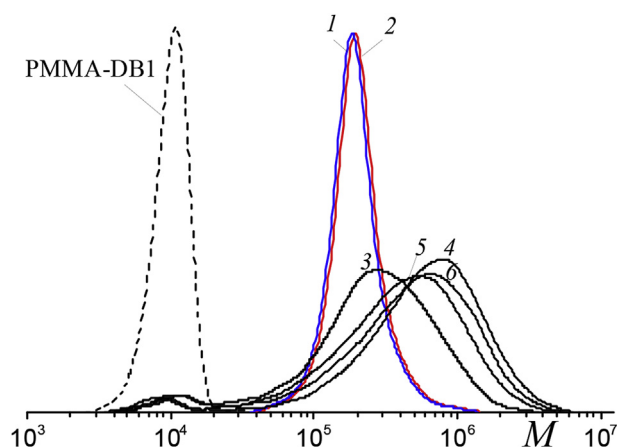


Fig. 4. Normalized SEC traces of the products of MMA polymerization conducted at 80 °C for 24 h with $[AIBN] = [PMMA-DB1] = 10^{-3}$ mol/L. Chain extension was tried with PMMA-DB1 without thermal treatment (1) and after storage at 100 (2), 120 (3), 140 (4), 160 (5) and 180 °C (6) for 24 h in inert atmosphere. SEC trace of the initial PMMA-DB1 (dashed) is given for comparison.

Table 3

Main characteristics of dithiobenzoate-terminated PMMA of various MM subjected to the thermal treatment for 24 h.

Sample	T, °C	M_n , g/mol	\bar{D}	Molar fraction of “living” chains, % ^a
PMMA-DB1 $M_n = 9600$	140	9800 ^b	1.11 ^b	21
PMMA-DB2 $M_n = 14000$	120	11400	1.08	20
	140	11600 ^b	1.09 ^b	18
		12400	1.09	<1
PMMA-DB3 $M_n = 29800$	120	29100	1.14	19
	140	28000 ^b	1.19 ^b	17
		28800	1.14	<1

^a The concentration of “living” chains was determined by UV–vis spectrometry.

^b Polymers were kept at the specified temperature for 4 h.

dispersity might originate from a pronounced autoacceleration of the polymerization due to the square-law termination of propagating radicals, which is typical of MMA polymerization mediated by dithiobenzoates taken at low concentrations [47]. In all other cases, an increase in the thermolysis temperature (140–180 °C) also results in a bimodal MMD of the resulting polymers (curves 4–6). The oligomeric mode corresponds to unreacted initial pre-heated PMMA-DB1 macromolecules taken for chain extension, while the high molar mass mode describes the polymerization product with a broader MMD. Being in agreement with the spectroscopic data, these results also lead to the conclusion about complete cleavage of dithiobenzoate groups in PMMA during its prolonged thermolysis at 140 °C and above.

An increase in the MM of dithiobenzoate-terminated PMMA has

no effect on its thermal stability, which was examined at 120 and 140 °C during 24 h (Table 3). The similar data were obtained after heating the polymers for 4 h at 140 °C. This result seems reasonable, as the cleavage of a dithiobenzoate group is a monomolecular reaction [27], which should not be affected by the polymer length.

3.2.2. Poly(methyl methacrylate) with trithiocarbonate end-group

The thermolysis of dodecyl trithiocarbonate-terminated PMMA (PMMA-TC2) in the temperature range of 100–180 °C varies from that of PMMA with a dithiobenzoate end-group. Decoloration of PMMA-TC2 from yellow to white occurs at lower temperatures (Fig. S3). Whereas the polymer keeps a unimodal MMD, its average MM slightly decreases with increasing the thermal stress temperature (Table 4).

The molar concentration of dodecyl trithiocarbonate groups in the polymer and the molar fraction of “living” chains were determined by UV–vis spectroscopy in THF as described above. Both low molar mass RAFT agent and PMMA-TC2 taken at equal concentrations demonstrate similar absorption spectra with an intense maximum at 310 nm (Fig. 5a). This allows using the molar extinction ratio of CPDTC, $\epsilon = (10.2 \pm 0.9) \times 10^3$ mol/(L × cm), for further calculations. The intensity of the absorbance maximum for PMMA-TC2 decreases rapidly with increasing the thermal stress temperature (Fig. 5b).

After heating PMMA-TC2 for 24 h at 100 °C, the intensity of the absorbance maximum falls by half, whereas heating at 120 °C completely terminates absorption. The results of the spectra analysis are summarized in Table 4. Evidently, the long-term thermal stability of PMMA-TC2 is noticeably lower than that of PMMA-DB1 and even a partial loss of terminal dithiobenzoate functionality at 100 °C should become apparent in the chain extension experiments.

Indeed, according to the SEC data, the chain extension of PMMA-TC2, pre-heated for 24 h at 100 °C, with MMA results in a bimodal MMD. The oligomeric mode corresponds to unreacted PMMA-TC2 chains with lost RAFT functionality, whereas the second mode describes the polymerization product with a relatively broad MMD and M_n close to that of the chain-extended non-thermolized PMMA-TC2 (Fig. 6, curve 2, Table 4). At the same time, the initial PMMA-TC2 successfully undergoes chain extension and yields PMMA with a narrow MMD (curve 1). At higher temperature of the thermal stress, chain extension is replaced with conventional radical polymerization that results in the formation of a polymer with higher MM and broader MMD (curves 3–6, Table 4).

As in the case of PMMA-DB, the polymerization degree of PMMA-TC has no visible effect on the thermal stability of the polymer. As is seen from Table 5, in all the cases a slight decrease in M_n is observed and the molar fraction of “living” chains after the thermal stress of similar duration is about the same value. A typical transformation of the MMD of PMMA-TC is presented in Fig. 7 for PMMA-TC1 isothermally stored at 120 °C for different times. Longer

Table 4

Main characteristics of PMMA-TC2 subjected to the thermal treatment for 24 h and further chain extension.

T, °C	M_n , g/mol	\bar{D}	$[-SC(=S)S-C_{12}H_{25}]^a$, mol/L	Molar fraction of “living” chains %	Chain extension	
					$M_n \times 10^{-3}$, g/mol	\bar{D}
—	14900	1.25	1.54×10^{-4}	100	200 ^b	1.24
100	15300	1.27	0.72×10^{-4}	46	200	1.97
120	15200	1.27	5×10^{-6}	3	550	1.90
140	14700	1.26	5×10^{-6}	3	610	2.12
160	14300	1.27	3×10^{-6}	2	600	2.30
180	13600	1.28	2×10^{-6}	1	600	2.50

^a The concentration of “living” chains was determined by UV–vis spectrometry.

^b Theoretical value of M_n is 190 000 g/mol.

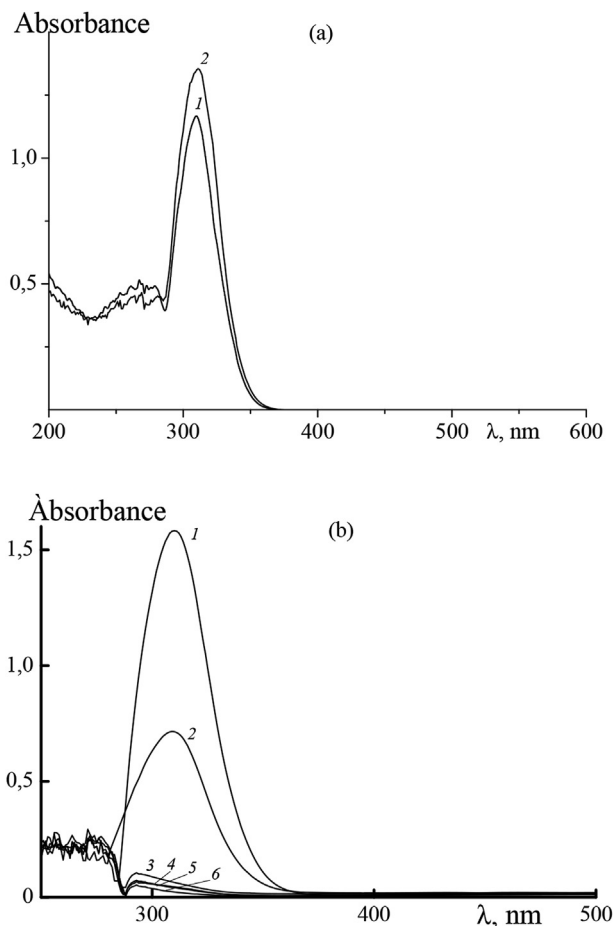


Fig. 5. UV–vis spectra of (a) CPDTC (1) and PMMA-TC2 (2) in THF at 25 °C and of (b) PMMA-TC2 without thermal treatment (1) and after 24 h storage at 100 (2), 120 (3), 140 (4), 160 (5), and 180 °C (6) in inert atmosphere.

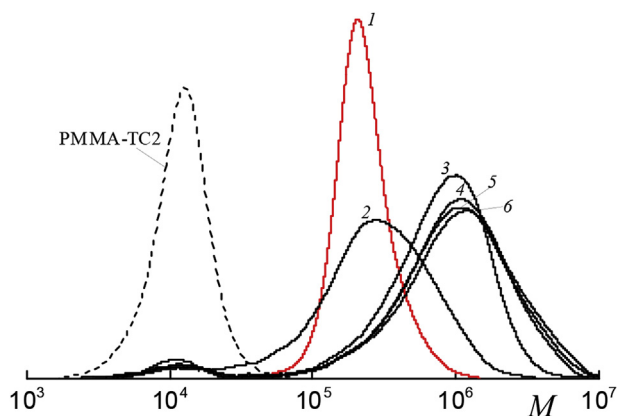


Fig. 6. SEC traces of PMMA-TC2 chain-extended without thermal treatment (1) and after 24 h storage in inert atmosphere at 100 (2), 120 (3), 140 (4), 160 (5), and 180 °C (6) normalized to the unit area. MMA polymerization was conducted at 80 °C for 24 h at $[AIBN] = [PMMA] = 10^{-3}$ mol/L. SEC trace of the initial PMMA-TC2 (dashed) is given for comparison.

heating causes a slight shift of the SEC trace toward the low molar mass region.

3.2.3. Kinetics of isothermal thermolysis

Molar mass effect on the kinetics of dithiobenzoate group

Table 5

Main characteristics of dodecyl trithiocarbonate-terminated PMMA of various MM subjected to the thermal treatment for 24 h.

Sample	T , °C	M_n , g/mol	\bar{D}	Molar fraction of “living” chains, % ^a
PMMA-TC1	120	7200 ^b	1.19 ^b	47
$M_n = 7700$ g/mol				
PMMA-TC2	120	12900 ^b	1.22 ^b	57
$M_n = 14900$ g/mol				
PMMA-TC3	120	28000 ^b	1.19 ^b	55
$M_n = 33600$ g/mol	140	28500	1.22	<10
		22500	1.36	<1

^a The concentration of “living” chains was determined by UV–vis spectrometry.

^b Polymers were kept at the specified temperature for 4 h.

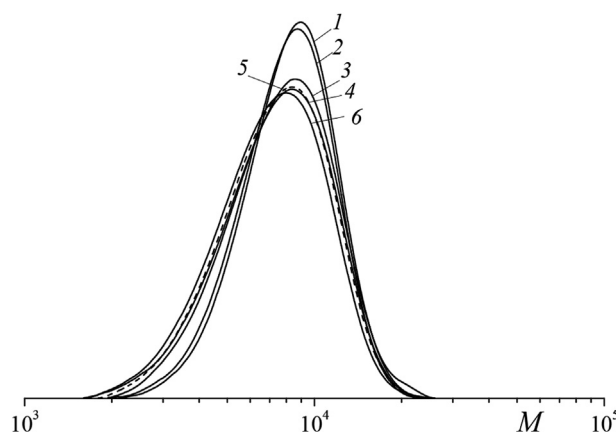


Fig. 7. SEC traces of PMMA-TC1 chain-extended without thermal treatment (1) and after storage for 20 (2), 40 (3), 60 (4), 120 (5), and 240 min (6) at 120 °C.

elimination was studied for PMMA-DB1, PMMA-DB2, and PMMA-DB3 polymers at 140 °C, when their thermolysis proceeds at a noticeable rate but MM remains nearly unchanged. Preliminarily degassed ampoules containing a given mass of each polymer were stored for a prescribed time at 140 °C, then dissolved in acetone, precipitated in methanol, dried in vacuum, and analyzed by UV–vis spectrometry. The corresponding absorption spectra are shown in Supplementary data as Fig. S4. Dividing the peak values by the molar extinction ratio of 1.6×10^4 mol/(L \times cm) listed in Experimental section, we obtain the current concentration of dithiobenzoate groups.

Fig. 8 presents the semi-logarithmic time dependences of the dithiobenzoate group concentration in three PMMA samples of different MM that were subjected to the isothermal treatment. All the data are satisfactorily described with straight lines thus corroborating the supposed unimolecular thermal degradation mechanism in dithiobenzoate-terminated PMMA [27]. Within the experimental error, all these lines have the same slope of $(1.2 \pm 0.1) \times 10^{-4} \text{ s}^{-1}$, which means that the degradation rate is independent of the molar mass of PMMA.

The same technique was applied for studying the thermolysis kinetics of dodecyl trithiocarbonate end-groups in PMMA-TC1, PMMA-TC2, and PMMA-TC3 samples isothermally stored at 120 °C. The lower treatment temperature was chosen due to the weaker thermal stability of TC end-groups compared with DB-ones, which was established in the preliminary dynamic experiments (Fig. 1a). The absorption spectra of PMMA-TC polymers are plotted in Supplementary data as Fig. S5. It is seen that after 6 h of treatment at 120 °C the concentration of Z-groups in PMMA decreased not more than twice.

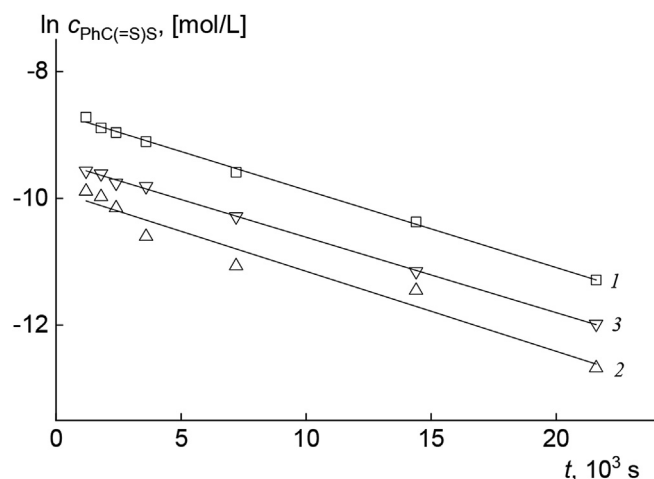


Fig. 8. Dithiobenzoate group concentration in PMMA-DB1 (1), PMMA-DB2 (2), and PMMA-DB3 (3) polymers stored for time t at 140 °C.

Using the molar extinction ratio of 1.02×10^4 mol/(L × cm), the time dependences of the dodecyl trithiocarbonate group concentration were found. They are not linear in the semi-logarithmic coordinates so that the thermal degradation in this case cannot be considered as a first-order reaction (Fig. 9a). It is interesting that the TC-group degradation kinetics is linear in the double-logarithmic coordinates (Fig. 9b), which means that the concentration of TC-groups in the studied time range drops as $C_{SC(=S)S} \sim t^{-\alpha}$, where $\alpha = 0.12 \pm 0.01$ and 0.12 ± 0.02 for PMMA of the middle and highest MM, respectively, and $\alpha = 0.25 \pm 0.01$ for the shortest PMMA. As a mere speculation, we can suppose that the faster degradation rate in the latter case is conditioned by conformational factors.

We also studied the temperature effect on the degradation kinetics of trithiocarbonate groups in PMMA (Fig. 10). At 120 °C the kinetic curve 1 can be fitted with straight lines of different slope at the early and late stage of the reaction. Such behavior means the presence of fast and slow degradation processes and it can be interpreted taking into account the structure of TC group, which contains two C–S bonds compared to one such bond in a DB-group. One C–S bond is attached to a PMMA chain and another one to a long alkyl substituent. It may be supposed that they break up with different rates and, what is more important, alkyl tail elimination considerably changes the reaction rate for the other C–S bond due to a rearrangement of the remaining moiety. Let us formalize this as follows. The direct elimination of the functional end-group from the

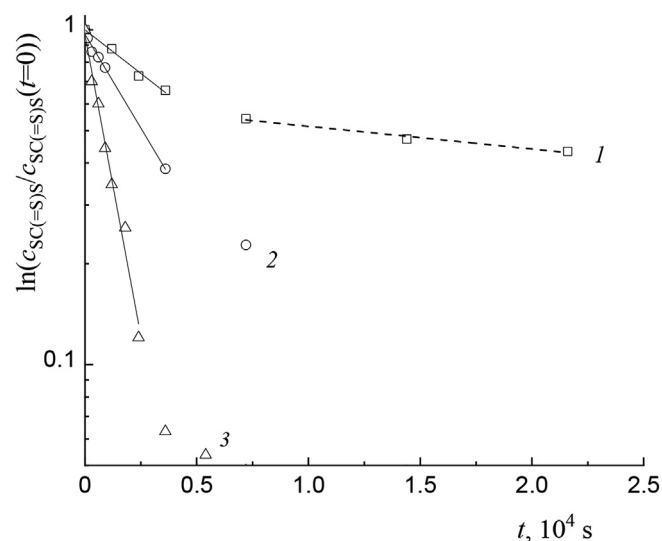


Fig. 10. Dodecyl trithiocarbonate group concentration in PMMA-TC1 polymer stored for time t at 120 (1), 140 (2) and 160 °C (3) in semi-logarithmic coordinates.

polymer proceeds with the rate constant k_1 , as shown in Scheme 2.

Alternatively, a two-step process occurs that includes elimination of alkyl $C_{12}H_{24}$ with the rate constant k_1^* and subsequent cleavage of the remaining C–S bond with the rate constant k_2 (see Scheme 3).

Note that the alkene tail removal is not detected by UV–vis spectroscopy, which measures the concentration of $SC(=S)S$ groups, c , attached to PMMA chains. Assuming the first order for all three elementary reactions, we easily get

$$c = c_0 \left[\frac{k_1 - k_2}{k_1 + k_1^* - k_2} \exp(-(k_1 + k_1^*))t + \frac{k_1^*}{k_1 + k_1^* - k_2} \exp(-k_2 t) \right],$$

where $c_0 = c(t=0)$.

At 120 °C we can use the linear segment of curve 1 for small t in Fig. 10 to find that $k_1 + k_1^* = (5.2 \pm 0.4) \times 10^{-5} s^{-1}$ and the second linear segment of the same curve to estimate $k_2 = (6.8 \pm 1.0) \times 10^{-6} s^{-1}$. Thus, the alkyl tail elimination slows down the degradation of the TC end-group by the order of magnitude. Note that the value of $k_1 + k_1^*$, which is the full rate of C–S bond splitting in PMMA-TC, is close to the value of $4.05 \times 10^{-5} s^{-1}$ found

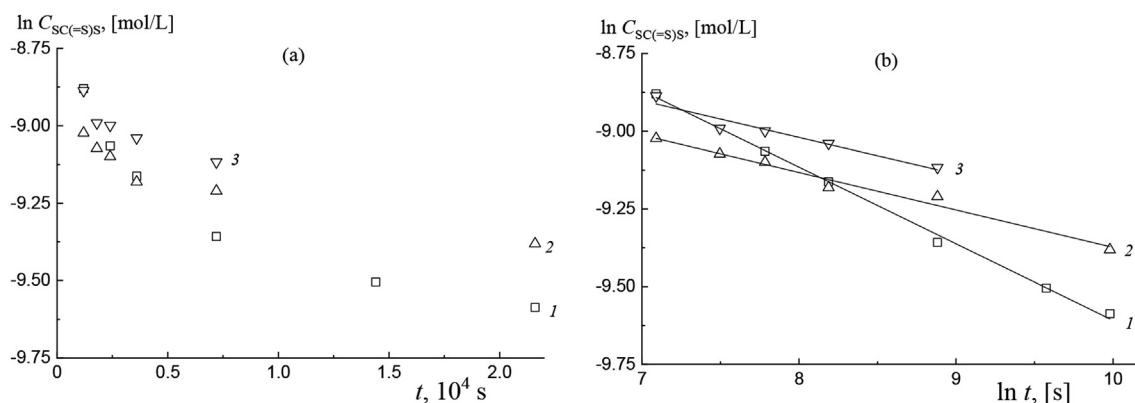
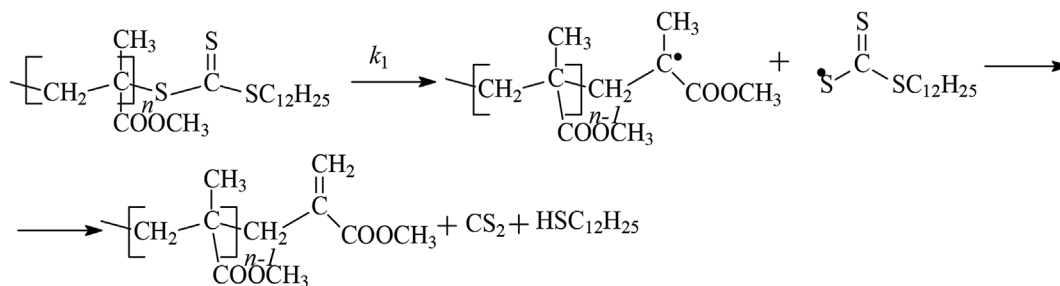
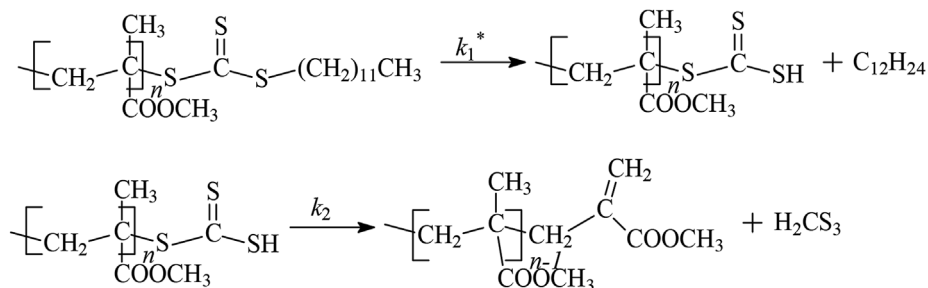


Fig. 9. Dodecyl trithiocarbonate group concentration in PMMA-TC1 (1), PMMA-TC2 (2), and PMMA-TC3 (3) polymers stored for time t at 120 °C in semi-logarithmic (a) and double-logarithmic coordinates (b).



Scheme 2. Single-step route of the end-group elimination in PMMA-TC.



Scheme 3. Two-step route of the end-group elimination in PMMA-TC.

in ref. 32 for the dithiobenzoate group cleavage in PMMA-DB at the same temperature. Using the linear fits for curves 2 and 3 in Fig. 10 we can estimate that $k_1 + k_1^* = (1.12 \pm 0.04) \times 10^{-4} \text{ s}^{-1}$ at 140 °C and $(3.3 \pm 0.1) \times 10^{-4} \text{ s}^{-1}$ at 160 °C. The former value is also close to $(1.2 \pm 0.1) \times 10^{-4} \text{ s}^{-1}$ found in this study for PMMA-DB at 140 °C. Therefore, the first step of the end-group elimination proceeds similarly in RAFT-synthesized PMMA-TC and PMMA-DB.

Since $k_2 \ll k_1 + k_1^*$, there are fast and slow elimination stages and the relative contribution of the slow process is determined by the ratio $k_1^*/(k_1 + k_1^*)$. As follows from Fig. 10, at 120 °C and even at 140 °C this ratio is not small, which means that k_1 and k_1^* are of the same order. However, at 160 °C the slow process becomes negligible, which corresponds to the case $k_1 \gg k_1^*$. It leads to the conclusion that the activation energy of C–S bond cleavage in PMMA-TC is higher for the bond connecting the thio group with PMMA compared with that for the bond connecting it with the alkyl tail. A quantitative estimate cannot be made using the available experimental data. Anyway, such peculiarities become unimportant above 160 °C, when the elimination of end-groups from PMMA-TC and PMMA-DB proceeds in one step.

4. Conclusions

Using PMMA of several MM with dithiobenzoate and trithiocarbonate end-groups, we have demonstrated that an accurate and systematic investigation avoids a number of controversial conclusions which can be found in the literature on the thermal stability of RAFT polymers being caused by insufficient control of polymer purity and aging.

Though PMMA-DB polymers appear to be generally more stable than PMMA-TC ones, none of them is able to keep its $-\text{SC}(=\text{S})-\text{Z}$ functionality, i.e. the ability to promote controlled chain extension, after a day of storage in inert atmosphere at a temperature above 120 °C. The end-group degradation starts with the homolysis of C–S bond, which proceeds as a monomolecular first-order reaction. The rate of homolysis, as well as the rate of PMMA chain degradation that takes place above 200 °C, depend on the nature of the Z-

group rather than on the MM of the polymer. Since a trithiocarbonate group contains two C–S bonds that can cleave at different rates and change the reactivity of the remaining C–S bond, the apparent kinetics of TC end-group elimination is more complicated compared with that of DB end-groups.

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Appendix A. Supplementary data

Supplementary data available: Estimation of the molar extinction ratios for two commercial RAFT agents, pictures and UV–vis spectra of the dithiobenzoate- and trithiocarbonate-terminated PMMA before and after isothermal treatment.

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.polyimdeggradstab.2019.03.017>.

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