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Short communication

SHORT COMMUNICATION

The thermal stability of poly(methyl methacrylate) prepared by RAFT polymerisation

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Abstract: Poly(methyl methacrylate), PMMA, was prepared by reversible addition–fragmentation chain transfer, RAFT, polymerisation using 2-(2-cyanopropyl)-dithiobenzoate, CPDB, as the RAFT agent. The thermal stability of the resulting polymer approached that of anionically prepared PMMA, as determined by thermogravimetry. This was the consequence of the RAFT prepared polymer having no head-to-head links and no chain end double bonds, which are responsible for the relatively low thermal stability of radically prepared PMMA.

Keywords: thermogravimetry; stability; RAFT; PMMA.

INTRODUCTION

The controlled (living) radical polymerisation, CLRP, of a wide variety of monomers has received considerable interest in recent years as the resulting polymers have very narrow molar mass distributions (approaching those of ionically prepared polymers but with less stringent polymerization conditions) and, due to the living nature of the polymerisations, copolymers of well defined structure are readily obtainable. The four distinct mechanisms usually employed to date for controlling radical polymerizations are nitroxide-mediated polymerisation, NMP,¹ atom transfer radical polymerisation, ATRP,² reversible addition–fragmentation chain transfer polymerisation, RAFT³ and interchange of xanthates, MADIX.⁴

RAFT Polymerisation is the most recently developed of these methods and has evolved as one of the most versatile of the CLRP techniques, the other being MADIX, because of its high tolerance to a wide variety of monomers and the mild conditions required.

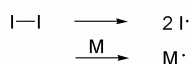
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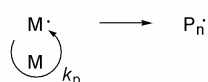
doi: 10.2298/JSC0809915K

As can be seen from Scheme 1, classical radical–radical termination does not occur in RAFT polymerisations, the isolated polymer is dormant with the RAFT agent attached to the ends of the chains. Thus, thermally weak links, *i.e.*, head-to-head bonds and chain end unsaturation, present in conventional radically prepared polymers due to termination by radical–radical coupling and disproportionation, respectively, should be absent in RAFT prepared polymers. Then, if the thermal stability of a polymer is governed by such weak links, the RAFT prepared polymers should be more stable than the conventionally prepared polymers.

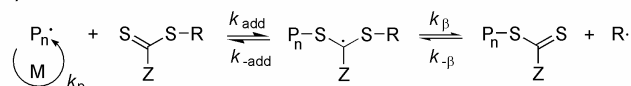
(i) Initiation



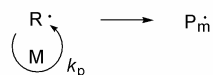
(ii) Propagation



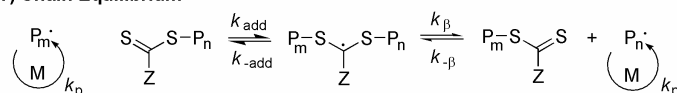
(iii) Chain Transfer



(iv) Reinitiation and Propagation



(v) Chain Equilibrium



Scheme 1.

Radically prepared poly(methyl methacrylate) (PMMA) is known to thermally degrade by depolymerisation to yield almost exclusively monomer.⁵ In spite of this, free radically prepared PMMA degrades in three distinct temperature regions depending on the mode of initiation of depolymerisation. Thus, in order of increasing temperature, depolymerisation of PMMA is initiated by scission of head-to-head bonds, scission of the β -bond to chain end unsaturation and main chain scission.⁶ On the other hand, anionically prepared PMMA has no weak links arising during termination and hence only main chain scission initiates thermal depolymerisation.

The aim of this study was to determine the thermal stability of PMMA prepared by the RAFT mechanism. To the best of our knowledge this is the first purpose designed study of the thermal stability of a polymer prepared by the RAFT mechanism.

EXPERIMENTAL

Methyl methacrylate (Fluka) was distilled under reduced pressure after removal of the inhibitor with a 5.0 % aqueous NaOH solution. Azobis(isobutyronitrile), AIBN, (Aldrich), employed as the initiator, was recrystallised from methanol. Benzene, thiophene free, (Fluka) was distilled before use.

The RAFT agent, 2-(2-cyanopropyl)-dithiobenzoate (CPDB), was prepared by a method described in the literature.⁷ It should be mentioned here that the yields of the RAFT agent were extremely low when a chromatographically pure substance was obtained. The structure of the RAFT agent was confirmed by ¹³C-NMR spectroscopy using a Varian-Gemini-200 (200 MHz) instrument.

The RAFT polymerisation was performed in an ampoule containing MMA 30 ml (0.28 mol), benzene 10 ml (0.11 mol), AIBN 40 mg (0.24 mmol) and CPDB 104 mg (0.470 mmol). The ampule was bubbled with N₂ for 15 min and sealed under vacuum and placed in a water bath at 60 °C. After 16 h, the reaction mixture was poured into methanol containing 5.0 % water. The polymer sample was reprecipitated from a benzene solution into methanol containing 5.0 % water and dried to constant mass at room temperature under vacuum. The percent conversion was determined gravimetrically.

The RAFT agent was removed from the PMMA samples by dissolving 0.50 g of the polymer in 40 ml toluene. AIBN (10 g) was added to this solution and, after removal of oxygen, the solution was heated at 80 °C for 3 h.⁸ The polymer was precipitated into methanol containing 5.0 % water and dried to constant mass at room temperature under vacuum.

The conventional radical polymerisation of MMA was performed in an ampoule containing MMA and AIBN at a molar ratio of MMA:AIBN of 25. The ampoule was bubbled with nitrogen and sealed under vacuum. The polymerisation lasted 15 min at 60 °C. The anionically prepared sample was obtained from PSS Polymer Standards Service GmbH, Mainz, Germany.

The number and weight average molar masses, M_n and M_w , respectively, and the polydispersity index, PD , of the obtained polymers and the polymer standard were determined at 30 °C by gel permeation chromatography, GPC, using a Waters instrument fitted with four analytical columns (Waters HR 2, HR 3, HR 4 and HR 5E) and a refractive index detector. Chloroform was used as the solvent at a flow rate of 1.0 ml min⁻¹. The obtained chromatograms were analysed with Waters Breeze software using a calibration curve of narrow molar mass distribution PMMA standards (PSS Polymer Standards Service GmbH, Mainz, Germany).

Non-isothermal, non-oxidative thermogravimetry, TG, and differential TG, DTG, was performed using a Perkin Elmer TGS-2 instrument in the temperature range 0–600 °C at heating rates of 2.5, 10, 20 and 40 °C min⁻¹, under a dynamic nitrogen flow (flow rate 26 ml min⁻¹).

RESULTS AND DISCUSSION

The ¹³C-NMR spectrum and the numbering of the C atoms of the prepared CPDE are shown in Fig. 1, from which it can be seen that all the expected peaks were present. No additional peaks were found in the spectrum, confirming that the sample was pure.

The polymer obtained after the RAFT polymerisation was pink due to the attachment of CPDB to the chain ends and had a weight average molar mass, M_w , of 3.59 kg mol⁻¹ and a polydispersity index, PD , of 1.19. After removal of the RAFT agent, the polymer was the normal white colour of precipitated PMMA.

The M_w of the polymer after removal of the RAFT agent remained unchanged and the PD decreased to 1.15.

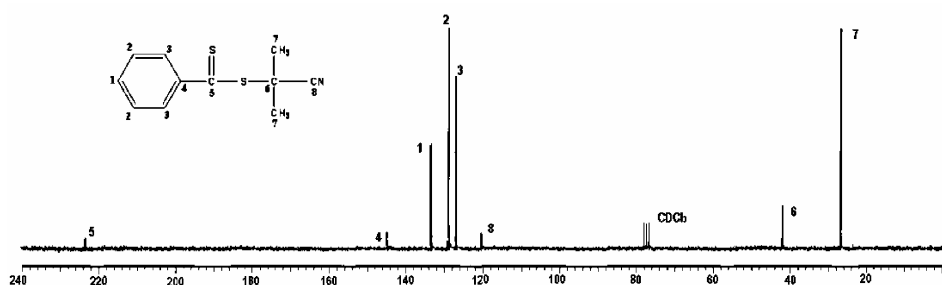


Fig. 1. ^{13}C -NMR Spectrum of CPDB (inset structure of CPDB with C atoms numbered).

The TG curves of the RAFT prepared PMMA sample at heating rates of 2.5, 10, 20 and 40 $^{\circ}\text{C min}^{-1}$ both before and after removal of the RAFT agent are shown in Figs. 2a and 2b, respectively. In both cases, the curves recorded at different heating rates run completely parallel to one another, showing that only one degradation mechanism was operative.

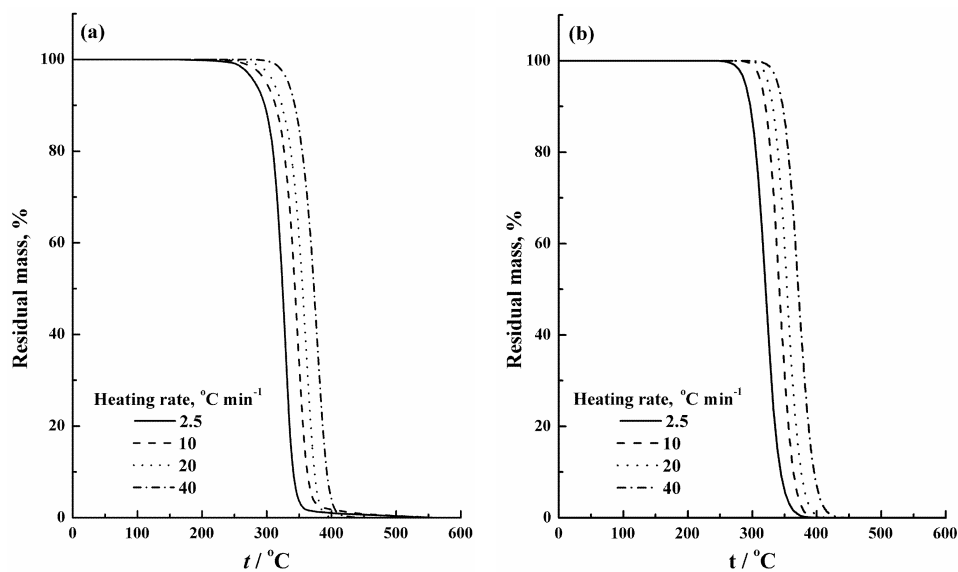


Fig. 2. TG Curves recorded at 2.5, 10, 20 and 40 $^{\circ}\text{C min}^{-1}$ of the polymer obtained after 16 h RAFT polymerisation both before (a) and after (b) removal of the RAFT agent.

In order to compare the TG curves of the examined polymers, the TG curves of each polymer recorded at 10 $^{\circ}\text{C min}^{-1}$ are presented in Fig. 3, together with those of an anionically and conventionally radically prepared PMMA samples of weight average molar mass 5.25 kg mol^{-1} (PD 1.04) and 4.46 kg mol^{-1} (PD 1.67), respectively, for comparison.

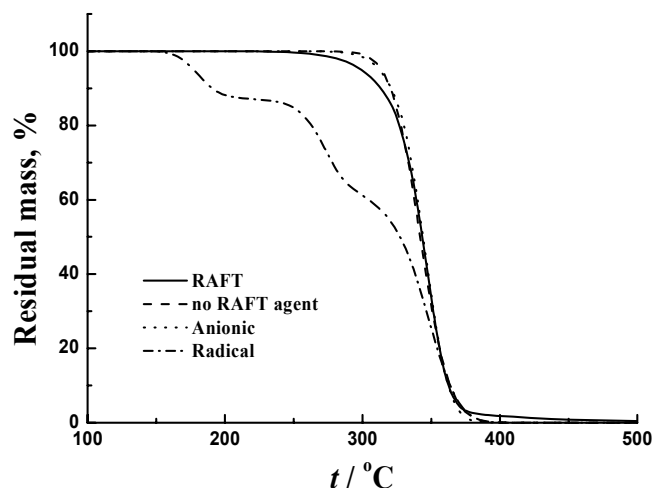


Fig. 3. TG curves recorded at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ of the polymer before and after the removal of the RAFT agent with the curves of an anionically and a conventional radically prepared polymer. The molar masses of the polymers were all comparable.

It is immediately visible that the RAFT prepared samples, both before and after removal of the RAFT agent, were considerably more stable than the radically prepared sample. Before removal of the RAFT agent, the polymer was less stable than after. This is probably due to the thermal degradation of the RAFT agent at the ends of the polymer chains. The mass loss commences slightly earlier with the PMMA with the RAFT agent still attached than after it had been removed and there is a high temperature tail visible on the TG curve. It would appear that the degradation of CPDB occurs in the same temperature range as main chain scission when it is attached to the end of the polymer chains. Thermal treatment has been used to remove the RAFT agent from polymers^{9,10} but not CPDB, which appears to be too stable for this method to be applicable. Most significantly, the TG curves of the RAFT prepared sample after removal of the RAFT agent and of the anionically prepared sample almost overlap. This means that the cyano-isopropyl groups from AIBN, which replaced the RAFT agent at the chain ends, did not initiate depolymerisation.

The characteristic mass loss temperatures, *i.e.*, the temperatures corresponding to 5, 10, 50 and 90 %, $T_{5\%}$, $T_{10\%}$, $T_{20\%}$, $T_{50\%}$ and $T_{90\%}$, respectively, for a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ are given in Table I. Again the similarity between the RAFT prepared PMMA after removal of the attached CPDB and the anionically prepared PMMA can be clearly seen.

These differences and similarities are even more visible in the DTG curves of the four polymers, shown in Fig. 4. Thus the DTG peaks at approximately 181 and 274 $^{\circ}\text{C}$ on the curve of the conventional radically polymerised PMMA arise

from depolymerisation initiated by the scission of the head-to-head bonds formed during chain termination by combination and from depolymerisation initiated by scission of the β -bond to the chain end vinylidene bonds formed during chain termination by disproportionation, respectively. The amount of degradation initiated by such weak links decreases as the molar mass of the polymer increases because their concentration in the polymer decreases. These weak bonds were obviously absent in the RAFT- and anionically-prepared polymers as only the DTG peak corresponding to main chain scission was present.

TABLE I. The temperatures of 5, 10, 20, 50 and 90 % mass loss for the examined PMMA samples

Synthesis method	$T_{5\%} / ^\circ\text{C}$	$T_{10\%} / ^\circ\text{C}$	$T_{20\%} / ^\circ\text{C}$	$T_{50\%} / ^\circ\text{C}$	$T_{90\%} / ^\circ\text{C}$
RAFT	298	312	327	342	363
RAFT removed	314	321	328	343	363
Anionic	311	321	330	345	363
Radical	176	191	263	328	363

As the RAFT mechanism is applicable under less stringent conditions than are required for anionic polymerisation, industrial samples of PMMA with improved thermal stability could be readily prepared using this method.

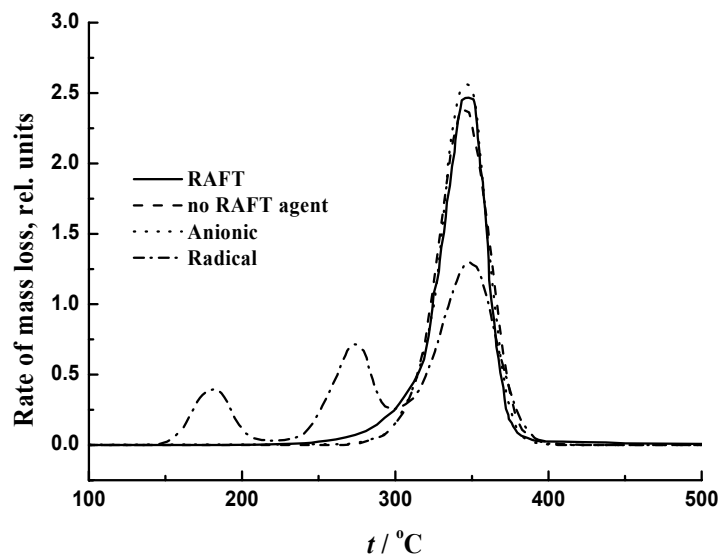


Fig. 4. The corresponding DTG curves of the TG curves shown in Fig. 3.

CONCLUSIONS

In conclusion, not only did the RAFT prepared PMMA have a narrow molar mass distribution, approaching that of anionically prepared PMMA, but also a significantly greater thermal stability than conventionally prepared polymers. It is to be expected that any polymer which can be successfully prepared

under controlled conditions and the thermal stability of which depends on the presence of weak bonds originating from radical–radical termination during its polymerisation, would also exhibit such an increase in thermal stability when prepared by the RAFT mechanism.

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ИЗВОД

ТЕРМИЧКА СТАБИЛНОСТ ПОЛИ(МЕТИЛ МЕТАКРИЛАТА)
СИНТЕТИСАНОГ RAFT ПОЛИМЕРИЗАЦИЈОМ

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Поли(метил метакрилат), РММА, је синтетисан контролисаном радикалном RAFT полимеризацијом, односно реверзибилном адитивно-фрагментационом трансфер полимеризацијом, у присуству 2-(2-цијанопропил)-дитиобензоата, CPDB, као RAFT агенса. Термичка стабилност РММА синтетисаног RAFT полимеризацијом је слична полимеру добијеном анјонском полимеризацијом, што је показала термогравиметријска анализа. РММА синтетисан RAFT полимеризацијом показује знатно бољу термичку стабилност у односу на РММА синтетисан полимеризацијом преко слободних радикала, због одсуства термички лабилних веза глава–глава остатака мономера у полимерном ланцу, као и двоструких веза на крајевима ланаца.

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