Polymer Communication

Control of methyl methacrylate radical polymerization via Enhanced Spin Capturing Polymerization (ESCP)

Lin Zang [a], Edgar H.H. Wong [a,c], Christopher Barner-Kowollik [a,*], Thomas Junkers [a,b,**]

[a] Preparative Macromolecular Chemistry, Institut für Technische Chemie und Polymerchemie, Karlsruhe Institute of Technology (KIT), Engesserstrasse 18, 76128 Karlsruhe, Germany
[b] Institute for Materials Research (IMO), Universiteit Hasselt, Agoralaan, Gebouw D, 3590-Diepenbeek, Belgium
[c] Centre for Advanced Macromolecular Design, The University of New South Wales, Sydney 2052, Sydney, Australia

ABSTRACT

The nitrone mediated polymerization of methyl methacrylate (MMA) via the enhanced (termination) spin capturing polymerization (ESCP) process is made possible via the addition of small amounts of styrene (between 5 and 10 vol.%) to the reaction mixture. Efficient control over the molecular weight between 7000 and 57,000 g mol^{-1} (at 60 °C) yields macromolecules that feature a mid-chain alkoxy-amine functionality and are rich in methyl methacrylate. The collated kinetic and molecular weight data allow for a deduction of the spin capturing constant, C_{SC}, in the range between 0.15 and 0.30. During the ESCP process, the number average molecular weight, M_n, of the formed mid-chain functional polymer is constant up to high monomer to polymer conversions (i.e. 80%). The high degree of alkoxyamine mid-chain functionality present in the generated polymeric material is evidenced via a subsequent nitroxide-mediated polymerization process employing the formed ESCP polymer, indicating a chain extension from 37,700 to 118,000 g mol^{-1} with a concomitant reduction in polydispersity (from 2.3 to 1.5).

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

Even with the established methods for controlled/living polymerization such as the reversible addition fragmentation transfer (RAFT) process [1], atom transfer radical polymerization (ATRP) [2] and nitroxide-mediated polymerization (NMP) [3], there is nevertheless a constant strive for the establishment of novel methods that efficiently control radical polymerizations. A recent enlargement of the polymer chemist's toolbox is the enhanced (termination) spin capturing polymerization (ESCP) method [4–6], which was developed on the basis of thioketone-mediated polymerization [7]. ESCP makes use of nitrones to control the functionality and the chain length of polymers obtained in-situ in a radical polymerization. Thereby, the addition of growing macroradicals to a nitrone is in competition with the addition of monomer units. When a propagating radical adds to a nitrone, chain growth of the macromolecule is stopped (hence the control over molecular weight of the obtained polymer depends on the concentration of the mediator)

and a macronitroxide is formed. These macronitroxides subsequently undergo a fast termination reaction in a second reaction step to form the final polymer product, representing macromolecules with a mid-chain alkoxyamine function. The general process is depicted in Scheme 1. The ESCP reaction is thus by itself a controlled, yet not a polymerization with living characteristics [4,6]. The product, however, is a polymer bearing an alkoxyamine in the middle of the chain and thus of a dormant nature. Therefore, release of macroradicals upon heating to higher temperatures (exceeding 100 °C) and subsequent chain extension in a conventional nitroxide-mediated polymerization is feasible.

We have recently demonstrated that ESCP functions efficiently and yields polymers with well-predictable molecular weight and high end group fidelity using various phenyl nitrones [5,8]. In addition, coupling of polymer chains that have been generated via ATRP was successful where the principle of ESCP is applied in the absence of monomer and thus growing chains [9]. So far, most examples of ESCP focused on polymers based on acrylates, styrene and N-isopropyl acrylamide as monomers. For these systems, good control was instantly achieved. As will be discussed below in detail, no successfully controlled polymerization of methacrylates have been reported to date. Polymerizations did occur in presence of nitrones, however, no effective control over molecular weight was observed. As methacrylates are however an important class of

* Corresponding author. Tel.: +49 721 608 5641; fax: +49 721 608 5740.
** Corresponding author. Tel.: +32 11 26 8318; fax: +32 11 26 8399.
E-mail addresses: christopher.barner-kowollik@kit.edu (C. Barner-Kowollik), thomas.junkers@uhasselt.be (T. Junkers).
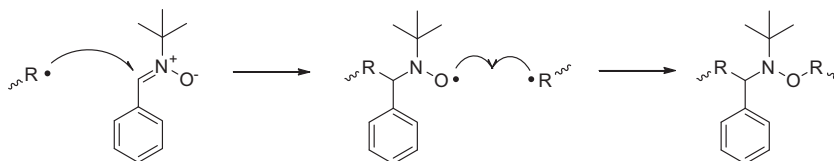
Scheme 1. Underpinning key reaction sequence in the Enhanced Spin Capturing polymerization (ESCP) process.

monomers, it is a matter of priority to explore avenues that overcome the existing limitations. In here, we report on the successful control of methyl methacrylate polymerization via usage of α-*tert*-butyl phenylnitrone (PBN, see Scheme 1), a nitrone that was previously employed in our studies to control other classes of monomers. The otherwise uncontrolled polymerization is converted into a controlled polymerization by adding small amounts of styrene to the polymerization mixture — a procedure that has also been used in the framework of conventional NMP of MMA [10–13].

2. Experimental section

2.1. Materials

Methyl methacrylate (MMA, Acros 99%) and styrene (STY, Acros 99%) were freed from inhibitor by percolating the monomer of a column filled with basic alumina. The initiator 2,2′-azobsisobutyronitrile (AIBN, Acros, 98%) was recrystallized twice from methanol. All chemicals for the synthesis of the nitrone were obtained from Sigma—Aldrich and used as received.

2.2. Preparation of α-phenyl-N-tert-butylnitrone (PBN)

18.94 g hydrogen peroxide urea adduct (UHP, 0.2 mol) dissolved in 100 mL methanol are added dropwise to a cooled solution of 16.33 g *N-tert*-butylbenzylamin (0.1 mol) and 13.20 g sodium tungstate) 0.04 mol in 150 mL methanol. The temperature of the reaction mixture is monitored and kept below 0 °C throughout the addition of the peroxide. Subsequently, the slightly yellow suspension is brought to ambient temperature and subsequently stirred overnight. The solvent is then removed in vacuo and dissolved in 200 mL dichloromethane. The residual solid is dissolved in 200 mL of water. The water phase is extracted with dichloromethane (3 × 150 mL) and the combined organic layers are then dried with sodium sulfate and the solvent is removed in vacuo. The pure nitrone α-phenyl-*N-tert*-butylnitrone (PBN) is directly obtained and no further purification is required. ^{1}H-NMR (250 MHz): $\delta = 8.22-8.18$ (m, 2H, 2H$_a$), 7.44 (s, 1H, H$_c$), 7.34–7.27 (m, 3H, 3H$_b$), 1.49 (s, 9H, -C(CH$_3$)$_3$). ^{13}C-NMR (75 MHz): $\delta = 28.3$, 70.5 (*N-tert*-butyl), 131.0 (CH=N), 130.0, 129.7, 128.7, 128.3 (Ph). The procedure was adapted from ref [14].

2.3. Synthesis of ESCP polymers

The initiator AIBN (0.067 g, 0.04 mol L^{-1}) is dissolved in 9.5 mL MMA and 0.5 mL styrene as well as the required amount of PBN are added to the mixture. The solution is then divided into 6 portions and filled into glass vials which are subsequently sealed by a rubber septum. Via purging the samples with nitrogen for approximately 10 min in an ice bath, oxygen is removed from the samples. The vials are subsequently placed into a pre-heated thermomixer at 60 °C. After predetermined reaction times the samples are removed from the heat and cooled down in an ice bath. The contents of the vials are transferred into aluminum pans and the conversion is determined gravimetrically by weighting the samples before and after evaporation of the residual monomer in a vacuum oven. To

avoid background polymerization, a solution of THF/hydroquinone is added to the pans after weighing. The samples are subjected to characterization without further treatment.

2.4. Block copolymer formation via NMP

The ESCP polymer (37,700 g mol^{-1}) obtained from a similar procedure as described above is precipitated in cold methanol to remove excess AIBN and PBN from the polymer. The obtained solid is then transferred into a Schlenck tube and dissolved in fresh styrene in a molar ratio of 1:3000 (100 mg copolymer in 1 mL fresh styrene). The tube is subsequently sealed and oxygen is removed via three freeze-pump-thaw cycles. For the NMP reaction, the tube is then brought into a pre-heated oil bath at 110 °C. After 100 min, the tube is removed from the oil bath and cooled down in an ice/water bath. The mixture is subsequently treated as the ESCP samples to isolate the polymer and to determine the polymer to monomer conversion.

2.5. Size exclusion chromatography

Gel Permeation Chromatography (GPC) measurements were performed on a Polymer Laboratories PL-GPC 50 Plus Integrated System, comprising an autosampler, a PLgel 5 μm bead-size guard column (50 × 7.5 mm) followed by one PLgel 5 μm Mixed E column (300 × 7.5 mm), three PLgel 5 μm Mixed C columns (300 × 7.5 mm) and a differential refractive index detector using THF as the eluent at 35 °C with a flow rate of 1 mL min^{-1}. The apparatus was directly calibrated using polyMMA standards ($M_p = 700 - 2\cdot106$ g mol^{-1}, PPS Mainz).

3. Results and discussion

MMA is not easily controlled via the NMP process. If carried out under standard reaction conditions, no control over molecular weight and functionality is observed over the course of the polymerization [15]. Two problems have been resolved over the years that prevent an effective living polymerization of methacrylates via nitroxide control. Firstly, the alkoxyamine bond that is formed upon the reaction between an active propagating radical and the nitroxide is not sufficiently stable to establish an effective equilibrium between active and dormant chains [15]. Thus, the reaction proceeds largely uncontrolled. Secondly, termination between growing chains and the controlling nitroxide may also occur via a disproportionation reaction, which is favored in methacrylate polymerizations in general [16]. Thereby, nitroxide is eliminated from the system — shifting the equilibrium towards the active radical and thus uncontrolled side — and irreversible terminated polymer chains are created. Two approaches have been used in the past to overcome this problem. Guillaneuf et al. [15] identified a nitroxide (i.e. 2,2-diphenyl-3-phenylimino-2,3-dihydroindol-1-yloxyl nitroxide, DPAIO) that forms sufficiently stable alkoxyamines with growing methacrylate chains and is at the same time sufficiently unreactive as to not undergo significant disproportionation reactions. In the second approach, Charleux and coworkers achieved control over methyl methacrylate polymerization using the

commercial SG1-nitroxide via addition of styrene as a comonomer in amounts between 4 and 8% [10]. Styrene as the comonomer has the function to allow for stable alkoxyamine bond formations upon reaction between a styrene-terminated growing chain and the control agent. As was demonstrated, only relatively small amounts of styrene are required to achieve conditions under which control over the polymerization is achieved. Thus, even though the obtained polymer contained a certain percentage of styrene, it is relatively close to pure polyMMA.

Inspired by the elegant copolymerization approach introduced by Charleux and colleagues [10], we in here evaluate the same approach for the control of MMA polymerizations via ESCP. The situation is here however somewhat different. No equilibrium between active and dormant species is established in ESCP and even if it is, the control over the polymerization is not compromised. In addition, disproportionation reactions only play a minor role. The reaction step that controls the molecular weight of the residual polymer is the addition of growing chains to the nitrone. The subsequent termination reaction has only a lesser impact on the size of the polymer. Disproportionation reactions affect the uniformity of functional groups, in contrast the molecular weight of combination and disproportionation products only differ by a factor of two. Nevertheless, addition of small amounts of styrene also has a beneficiary influence on the ESCP of MMA.

Fig. 1 depicts molecular weight distributions of poly(MMA-co-STY) polymers obtained from ESCP at low monomer conversions with various concentrations of PBN as control agent. For the sake of simplicity, mixtures of MMA and STY were made on a volume-basis. For the molecular weight distributions depicted in Fig. 1, the polymerizations were conducted with a content of 10 vol.% styrene in the reaction mixture, initiated by 0.04 mol L^{-1} AIBN. The nitrone concentration was varied between zero and 0.4 mol L^{-1} as indicated within the figure. As noted − for practical reasons − the experiments in the current work were carried out based on volume percentages. As the density and molar mass of both monomers are very similar, volume and mole percentages are very similar, too. Overall, a good control over molecular weight is achieved. The average molecular weight of the samples varies between 57,000 g mol^{-1} for the uncontrolled reaction (featuring a nitrone concentration of zero) and close to 7000 g mol^{-1} for the highest PBN concentration of 0.4 mol L^{-1}. The polydispersities range between 1.5 for the highest PBN content to about 1.8 at the lowest concentration, as is typical for ESCP polymers [5]. Thus,
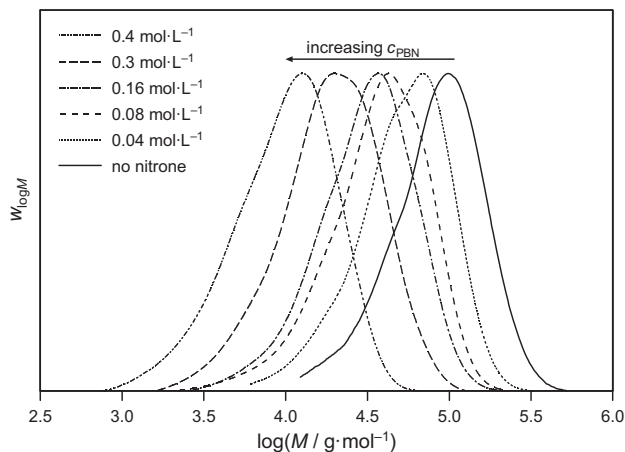
higher molecular weights are observed than for comparable monomers where average molecular weights between 2000 and 30,000 g mol^{-1} are commonly obtained [4,5]. Further, it can be observed that the molecular weight distributions are slightly bimodal. Closer inspection of the distributions (by differentiating the distributions and comparison of the thereby identified points of inflection) reveals that all distributions (also the one obtained in absence of PBN) are mixtures of two distributions differing in a factor of 2 in size. Thus, it may be concluded that the observed bimodality is a result from disproportionation reactions occurring during the polymerizations; clearly, the styrene content is not high enough to allow for almost exclusive termination by combination (of macronitroxides and growing macroradical chains). Regardless, the molecular weight control remains largely unaffected as discussed above.

From the obtained molecular weights, the rate of addition of the growing chains to the nitrone, $k_{ad,macro}$, and the so-called spin capturing constant C_{SC} (which is defined as the ratio of $k_{ad,macro}$ over the propagation rate k_p) can be derived in the following fashion

$$DP_n^{-1} \quad = \quad DP_\infty^{-1} \quad + \quad \frac{\lambda \cdot k_{ad,macro} \cdot c_{PBN}}{k_p \cdot c_M} \tag{1}$$

where DP_n^{-1} is the inverse of the degree of polymerization, DP_∞^{-1} the inverse of the degree of polymerization that is obtained in an uncontrolled reaction (zero nitrone concentration) and c_M is the monomer concentration. The factor λ was derived in our previous studies as 0.5 [4], which represents exclusive termination via combination (as is usually the case in ESCP). For termination exclusively via disproportionation, λ would reach unity. Thus, the true value for the polymerizations at hand is between 0.5 and 1 with the exact value being dependent on the styrene content as this will influence the number of possible disproportionation events.

Fig. 2 shows the data from Fig. 1 − transformed into average degrees of polymerization plotted against the nitrone concentration − in addition to a further data-set obtained with 5 vol.% styrene in the reaction mixture according to Equation (1). Both data sets display the same trend and may be regarded to be identical within the scatter of the data. From a joint fit the combined value of $\lambda \cdot C_{SC} = 0.15$ is obtained under the assumption of a monomer concentration of 9.0 mol L^{-1} (which is derived from the bulk density (0.90 g mL^{-1} at $T = 60\,°C$) [17] of MMA; as molecular weight and density of styrene and MMA are very similar (4% difference),

Fig. 1. Molecular weight distributions of polymer made via ESCP from MMA-STY copolymerizations at 60 °C with 10 vol.% styrene content and PBN as the mediating agent. All samples were taken at low (<5%) monomer to polymer conversions.
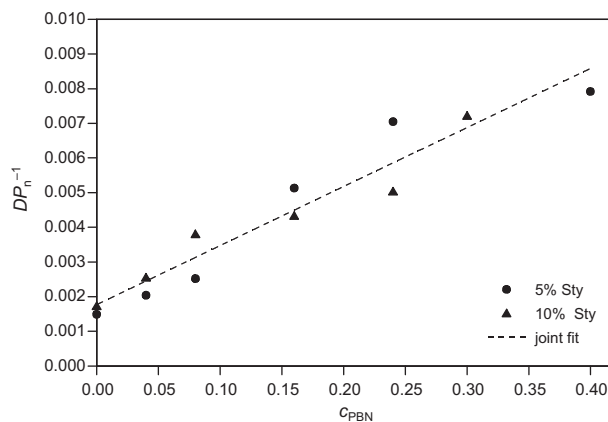

Fig. 2. Inverse of the degree of polymerization of low-conversion polymer samples taken from PBN-mediated polymerizations of MMA at 60 °C with 5 and 10 vol.% styrene content, respectively, as a function of PBN concentration. The straight line gives the joint fit to both data sets.

the error introduced via such an assumption is negligible). Thus, the λ-decoupled value of C_{SC} lies between 0.15 and 0.30. From this value, absolute addition rates of the propagating macroradicals to the nitrone can be estimated. The average propagation rate of MMA-STY copolymerizations at the given monomer composition at 57 °C is close 500 L mol^{-1} s^{-1} [18] from which an addition rate 75 L mol^{-1} s^{-1} < $k_{ad,macro}$ < 150 L mol^{-1} s^{-1} is derived.

Generally, the spin capturing constant, C_{SC}, is of higher practical value than the addition rate coefficient, $k_{ad,macro}$, because it directly allows for the prediction of the average molecular weight for any given nitrone concentration (so does $\lambda \cdot C_{SC}$ in case the ratio of combination to disproportionation does not change). Thus, an exact knowledge of $k_{ad,macro}$ is not strictly required and C_{SC} is sufficient. Even under the assumption of $\lambda = 0.5$, C_{SC} is 0.30 and hence very low compared to values obtained for the same parameter in the homo-polymerization of styrene [5], where a value of 1.7 (or a $k_{ad,macro}$ of 580 L mol^{-1} s^{-1}, respectively) was deduced at the same temperature. The propensity of a growing chain to add to PBN in the MMA/STY mixtures is thus about 5–10 times lower compared to styrene homopolymerization. Such a decrease can be explained via the assumption that growing chains with a MMA terminus do not effi-ciently add to the nitrone to form a nitroxide. Based on literature reactivity ratios of the styrene/MMA system ($r_1 = 0.493$ and $r_2 = 0.489$) [19], one can derive (via the Lewis–Mayo equation) that approximately 15% of all chains have a terminal styrene group for the 10% styrene mixture and about 10% of chains for the 5% styrene mixture. Thus, every chain must on average undergo 6 to 7 propa-gation steps before an addition to the nitrone can take place. If one additionally assumes that no penultimate unit effect occurs, the average addition rate in the MMA-STY copolymerization can be calculated based on the homopolymerization $k_{ad,macro}$. Following this assumption, an addition rate of approximately 90 L mol^{-1} s^{-1} is expected for the polymerization containing 10% styrene and about 60 L mol^{-1} s^{-1} for the 5% mixture. Both values are relatively close to the observed value provided above. Even though the pleasing agreement between the values might to some degree be coincidence, it may nevertheless be concluded that the assumption of an almost non-adding MMA chain terminus to the nitrone is largely valid. Such a conclusion is also in-line with the observation of completely uncontrolled polymerizations of MMA in the presence of PBN when no comonomer is added, which is to be expected when the nitrone does not take part in the reaction.

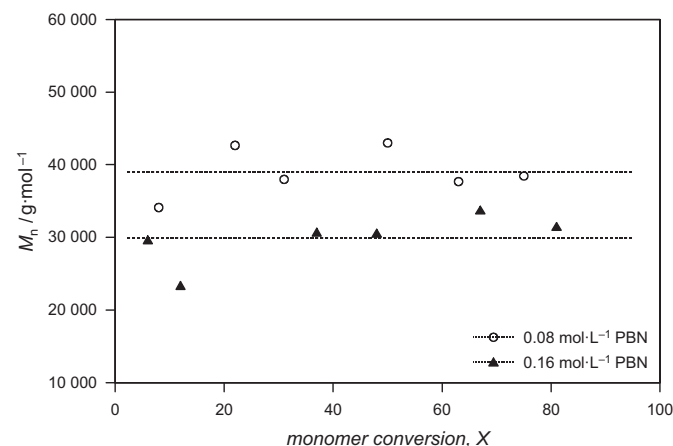Fig. 3 depicts the evolution of the molecular weight with increasing conversion for polymerizations with 5% styrene content at 60 °C controlled by 0.08 mol L^{-1} PBN and 0.16 mol L^{-1}, respec-tively. The samples shown in the figure were taken at different reaction times, where the longest reaction time was about 3.5 h in case of the sample at 80% monomer conversion for the higher PBN concentration. From a low C_{SC}, one would usually expect decreasing molecular weight with increasing nitrone concentration. The C_{SC} value determined above is however only an average value and the true value (if only chains are counted that have a terminal styrene group) is in fact closer to unity or slightly above. Thus, it comes as no surprise that throughout the polymerization an almost constant molecular weight is found. For the polymerization with a nitrone concentration of 0.08 mol L^{-1}, an average molecular weight of 39,000 g mol^{-1} is found in the conversion regime of up to 80% monomer consumption. For the doubled concentration of PBN, a decreased molecular weight is identified as expected at 29,900 g mol^{-1}. The reactivity ratios in the MMA-STY system are relatively close to an ideal copolymerization. Thus, no large composition drift occurs during the polymerization and the control over the reaction works as efficiently as at low conversions.

It should also be noted that the alkoxyamines formed during the ESCP with PBN may feature a comparatively high decomposition rate, thus leading to an NMP-like equilibrium at relatively low temperatures. However, the almost constant molecular weight with increasing monomer conversion demonstrates that this is – at least at 60 °C – not (yet) the case. A hybrid ESCP/NMP polymeri-zation may however occur when the temperature is increased.

The above observations all indicate that the control over molecular weight is reached in the copolymer system with qualitatively the same features as in conventional ESCP reactions with other monomers accompanied by the alteration of an overall reduction in the observable C_{SC}. While the above is a generally satisfying result, the question remains how well the functionality of the chains is controlled. As discussed above, one can expect that from disproportionation reactions unfunctional-ized chains are created that cannot be reactivated via the NMP mechanism.

A reliable way to test for the degree of functionality is to perform a chain extension via the NMP mechanism. After freeing the ESCP polymer from any excess nitrone and thermal initiator via precip-itation, fresh monomer is added to the isolated polymer and a NMP reaction is started via heating the sample to 110 °C. Under such conditions, only chains that carry an intact alkoxyamine function (hence chains that were formed upon combination of
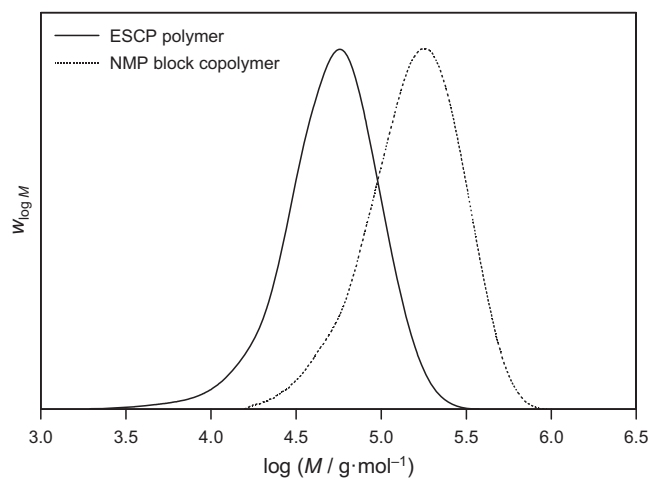

Fig. 3. Monomer to polymer conversion dependence of the number average molecular weight, M_n, in the bulk ESCP of MMA with 5 vol.% styrene content at 60 °C, mediated with PBN and initiated by 0.04 mol L^{-1} AIBN.

Fig. 4. Molecular weight distribution of polymer made via ESCP of MMA with 5 vol.% styrene as comonomer and the distribution of the polymer after reactivation of the alkoxyamine bonds at 110 °C and chain extension with pure styrene via NMP.

macronitroxides and growing chains) can be reactivated and chain extended. All other material is dead and will not react further. The outcome of such an assessment is depicted in Fig. 4. The full line provides the molecular weight distribution of polymer made under the same conditions as employed in the study of the conversion dependence with 0.08 mol L^{-1} PBN. The dotted line represents the distribution of polymer after NMP at 110 °C employing pure styrene as the monomer for chain extension. The fresh monomer was added in a ratio of 1:3000, based on the assumption of quantitatively mid-chain alkoxyamine functional ESCP polymer, i.e. featuring no functionality defects from disproportionation. The figure shows that an efficient chain extension has taken place and that the majority of polymers thus carried the required alkoxyamine functionality in the middle of their chains. The resulting polymer is thus of a triblock copolymer structure with the sequence p(MMA-co-STY)−pSTY− p(MMA-co-STY). The average molecular weight increased in the given example from 37,700 g mol^{-1} to 118,000 g mol^{-1}, which fits reasonably well with the theoretically expected molecular weight of 100,500 g mol^{-1} (based on the styrene monomer conversion of 19%). The polydispersity of the NMP-chain extended polymer reads 1.5, well below the value of 2.3 of the starting ESCP polymer, further attesting the living nature of the chain extension.

From the above experiment, one can conclude that a reasonably well functionalized polymer is obtained from ESCP despite the disturbing influences of disproportionation. The NMP-chain extended distribution shows however a (slight) tailing on the low-molecular weight side of the distribution, which indicates that a proportion of chains did not react in the NMP process. SEC only provides a mass-weighted distribution, thus a quantification of the percentage of chains that did not react is fraught with complications. Overall, it should be noted that more data is required to assess the efficiency of block copolymer formation and the current example is only meant to demonstrate that the ESCP polymer is of overall satisfying functional fidelity and that chain extensions can in principle be performed. Additionally, the chain extension allows for insights into the microstructure of the chains that have terminated the macronitroxide to form the alkoxyamine: Temperatures above 100 °C are required to perform the NMP reaction. If the alkoxyamine was formed upon reaction with a MMA-terminated macroradical, then much lower temperatures would be sufficient to start the homolysis of the C−O bond in the alkxoyamine. Thus, the required high temperature allows the conclusion that the terminating growing macroradicals must have had a styrene terminus while chains with a MMA terminal unit did not undergo a combination reaction. It may be speculated that chains with a MMA chain end form an alkoxyamine, yet that this bond is already too unstable at the synthesis temperature. Under these conditions, the chains would undergo reversible termination reactions until either a disproportionation event annihilates the spin or the macroradical adds a styrene unit when it is in its active form.

4. Conclusions

In the current contribution, we have demonstrated that enhanced (termination) spin capturing polymerization (ESCP) of methyl methacrylate is efficiently feasible via the addition of small amount of styrene (up to 10 vol.%) to the reaction mixtures. Mid-chain alkoxyamine functional (methyl methacrylate rich) copolymers of styrene and methyl methacrylate could be obtained with molecular weights ranging from over 50,000 to 7000 g mol^{-1}. Although the molecular weight distributions display a bimodality caused by the disproportionation events prevalent during the polymerization of MMA via the ESCP process, the molecular weight is constant as a function of the monomer to polymer conversion. These results indicate that the addition of small fractions of styrene to methyl methacrylate allows − similar to the previously demonstrated control of methyl methacrylate via NMP − for a functioning ESCP process. The kinetic and molecular weight data obtained in the present study allowed for the estimation of the spin capturing constant, C_{SC}, in between 0.15 and 0.30 at 60 °C. Importantly, the number average molecular weight as a function of monomer to polymer conversion remains constant up to high conversions (>80%), demonstrating that the process is capable of providing uniform polymeric material over a wide conversion range. The dormant nature of the ESCP generated poly(methyl acrylate)-co-polystyrene species was demonstrated via a subsequent chain extension by an NMP process at elevated temperatures, which afforded a triblock copolymer. Thus, the present contribution provides a convenient avenue for expanding the ESCP process to the important class of methacrylate-type monomer systems and allows for the macromolecular design of mid-chain functional alkoxyamine methyl methacrylate rich polymers.

References

[1] (a) Perrier S, Takolpuckdee P. J Polym Sci − Chem 2005;43:5347−93;
    (b) Moad G, Rizzardo E, Thang SH. Aust J Chem 2005;58:379−410;
    (c) Moad G, Rizzardo E, Thang SH. Aust J Chem 2006;59:669−92;
    (d) Moad G, Rizzardo E, Thang SH. Aust J Chem 2009;62:1402−72;
    (e) Barner-Kowollik C, editor. Handbook of RAFT polymerization. Weinheim, Germany: Wiley-VCH, ISBN 978-3-527-31924-4; 2008;
    (f) Barner-Kowollik C, Perrier S. J Polym Sci − Polym Chem 2008;46:5715−23.
[2] Matyjaszewski K, Xia J. Chem Rev 2001;101:2921−90.
[3] Hawker CJ, Bosman AW, Harth E. Chem Rev 2001;101:3661−88.
[4] Wong EHH, Junkers T, Barner-Kowollik C. J Polym Sci A Polym Chem 2008;46: 7273−9.
[5] Wong EHH, Stenzel MH, Junkers T, Barner-Kowollik C. J Polym Sci A Polym Chem 2009;47:1098−107.
[6] Junkers T, Wong EHH, Stenzel MH, Barner-Kowollik C. Macromolecules 2009; 42:5027−35.
[7] (a) Ah Toy A, Chaffey-Millar H, Davis TP, Stenzel MH, Izgorodina EI, Coote ML, et al. Chem Commun 2006:835−7;
    (b) Junkers T, Stenzel MH, Davis TP, Barner-Kowollik C. Macromol Rapid Commun 2007;28:746−53;
    (c) Günzler F, Junkers T, Barner-Kowollik C. J Polym Sci A Polym Chem 2009; 47:1864−76.
[8] Wong EHH, Stenzel MH, Junkers T, Barner-Kowollik C. Macromolecules 2010;43:3785−93.
[9] Wong EHH, Boyer C, Stenzel MH, Barner-Kowollik C, Junkers T. Chem Commun 2010;46:1959−61.
[10] Nicolas J, Dire C, Mueller L, Belleney J, Charleux B, Marque SRA, et al. Macromolecules 2006;39:8274−82.
[11] Nicolas J, Mueller L, Dire C, Matyjaszewski, Charleux B. Macromolecules 2009;42:4470−8.
[12] Nicolas J, Brusseau, Charleux B. J Polym Sci A Polym Chem 2010;48:34−47.
[13] Charleux B, Nicolas J, Guerret O. Macromolecules 2005;38:5485−92.
[14] Murahashi S, Mitsui H, Shiota T, Tsuda T, Watanabe S. J Org Chem 1990;55: 1736−44.
[15] Guillaneuf Y, Gigmes D, Marque SRA, Astolfi P, Greci L, Tordo P, et al. Macromolecules 2007;40:3108−14.
[16] Barner-Kowollik C, Vana P, Davis TP. The kinetics of free radical polymerization. In: Matyjaszewski K, Davis TP, editors. Handbook of radical polymerization. New York, NY: Wiley and Sons; 2002. p. 207.
[17] Brockhaus A, Jenckel E. Makromol Chem 1956;18:266−93.
[18] Coote ML, Zammit MD, Davis TP, Willet GD. Macromolecules 1997;30: 8182−90.
[19] Coote ML, Johnston LMP, Davis TP. Macromolecules 1997;30:8191−204.