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Sulfolane: an Efficient and Universal Solvent for Copper-Mediated Atom Transfer Radical (co)Polymerization of Acrylates, Methacrylates, Styrene, and Vinyl Chloride

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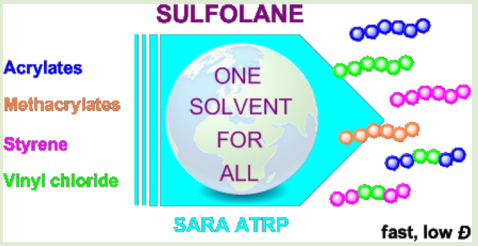
Supporting Information

ABSTRACT: A very fast and controlled atom transfer radical (co)-polymerization (ATRP) of acrylates, methacrylates, styrene, and vinyl chloride is reported in a single dipolar aprotic solvent, sulfolane, with the use of ppm amount of the copper catalyst. The observed rates of polymerization (k_p^{app}) of the monomers studied are similar to those reported using dimethyl sulfoxide (DMSO) and other polar solvents typically employed in single electron transfer (SET)-mediated atom transfer radical polymerization (ATRP) processes. As proof-of-concept, ABA type block copolymers of polystyrene-*b*-poly(vinyl chloride)-*b*-polystyrene and poly(methyl acrylate)-*b*-poly(vinyl chloride)-*b*-poly(methyl acrylate) were prepared for the first time using a reversible deactivation radical polymerization (RDRP) method in a single solvent. The quantitative preservation of halide chain-ends was confirmed by ^{1}H NMR and MALDI-TOF analysis as well as by the complete shift of the GPC traces. The results presented establish an innovative and robust system to afford a vast portfolio of (co)polymers in a single widely used industrial solvent.



Atom transfer radical polymerization (ATRP) is a versatile, efficient, and robust method that has opened unprecedented opportunities to synthesize (co)polymers with controlled molecular weight, composition, architecture, high chain-end functionality, and low dispersity (*Đ*).[1] ATRP is mediated by a dynamic equilibrium between dormant alkyl halide chains and growing radicals, which is catalyzed by a transition metal/ligand complex.[2] Traditionally, metal catalyst concentration greater than 10000 ppm were required to perform normal ATRP reactions. Recently, new variations of ATRP systems have been developed, namely, activators regenerated by electron transfer (ARGET) ATRP,[3] initiators for continuous activator regeneration (ICAR) ATRP,[4] electrochemically mediated (*e*-ATRP) ATRP,[5] and supplemental activator and reducing agent (SARA) ATRP.[6,7] These new techniques allow the use of very low concentrations of metal catalyst (<100 ppm), maintaining the control over the polymerization. Among these methods, SARA ATRP has demonstrated to be a very attractive technique using heterogeneous[7−9] zerovalent metal catalysts as both supplemental activator and reducing agent that can be easily removed from the reaction medium.[6−11] Also, Food and Drug Administration (FDA) approved inorganic sulfites, in combination with small amounts of soluble copper, proved to successfully mediate the SARA ATRP of several monomers in eco-friendly conditions.[12−16]

SARA ATRP has been used for the preparation of well-defined block copolymers in various solvents, such as water,[17] alcohol/water mixtures,[8,13,15,18] and anisole.[12] However, due to solubility issues and system particularities, it is sometimes difficult to find appropriate solvents to perform copolymerization of a wide range of monomers using the same ATRP system without polymer isolation.

The SARA ATRP (originally called as SET living radical polymerization or SET-LRP) of activated and nonactivated monomers catalyzed by copper complexes has become a very popular method for the preparation of complex polymer architectures. It should be noted that the proposed mechanisms of SET-LRP and SARA ATRP processes are based on the same elemental microsteps,[19] the only difference being the identification of the major/minor contributing reactions.

Dimethyl sulfoxide (DMSO) has proven to be a suitable solvent for the SARA ATRP of methyl acrylate (MA)[20] and methyl methacrylate (MMA),[20] as well as for the nonactivated monomer vinyl chloride (VC).[20] For the polymerization of other relevant monomers such as styrene (St), DMSO is not an appropriate solvent due to the very poor solubility of polystyrene in this solvent. Usually, St is polymerized in dimethylformamide (DMF),[7] toluene,[21] anisole,[22] or in bulk.[22] Thus, the possibility of having a single universal solvent for the preparation of well-defined block copolymers able to polymerize a wide range of monomer families is highly desirable. Another disadvantage of using DMSO in ATRP reactions is the

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very low efficiency of universal ATRP initiators such as sulfonyl chloride derivatives (e.g.: tosyl chloride), due to their rapid reaction at room temperature.[23] Since the first report of ultrafast synthesis of high molar mass polymers mediated by SET-LRP in DMSO, the careful selection of solvent in addition to metal catalyst/monomer/initiator/polymer systems has become a very important issue for the successful control of ATRP polymerization.

Sulfolane (2,3,4,5-tetrahydrothiophene-1,1-dioxide) is a dipolar aprotic industrial solvent commonly used in organic synthesis, gas purification and oil refining.[24] This solvent is completely miscible with water and with most polar and several nonpolar solvents (except alkanes). It is also completely miscible with aromatic hydrocarbons and can also dissolve polystyrene. Compared to other dipolar aprotic solvents, sulfolane presents several advantages, such as high dipole moment, high relative permittivity and a high Hildebrand solubility parameter.[2,8,9,15,24,25] Therefore, an elevated solvency power for the reactions involving polarizable intermediated (like in SET mediated reactions, for example) is expected when using sulfolane as the solvent. Sulfolane is also very stable toward various reactive organic and inorganic solvents and reagents and has the lowest penetration trough skin parameter (compared to other dipolar aprotic solvents).[24] While sulfolane is widely used in organic synthesis and step-growth polymerizations in place of DMSO, DMF, or other solvents, this solvent has never been reported as a suitable solvent for the ATRP or related developments.

In this communication, we present for the first time the use of sulfolane as the single solvent for the successful Cu(0)-mediated SARA ATRP of MA, MMA, St and VC. Several reaction parameters were investigated in the polymerization of each monomer to allow good control. As a proof-of-concept, the reported system was used to prepare PMA-*b*-PVC-*b*-PMA (PMA: poly(methyl acrylate); PVC: poly(vinyl chloride)) and PS-*b*-PVC-*b*-PS (PS: polystyrene) block copolymers.

Preliminary experiments were carried out for the SARA ATRP of MA catalyzed by Cu(0) wire in sulfolane (Table S1, entries 1–3, and Figure 1). For the purpose of comparison, DMSO was also used under the same reaction conditions because this solvent is often used in the SARA ATRP of the most studied model monomers MA, MMA, and VC (by the so-called SET-LRP).[2,6,20] The results presented in Figure 1 show that the level of control achieved is similar for both solvents,

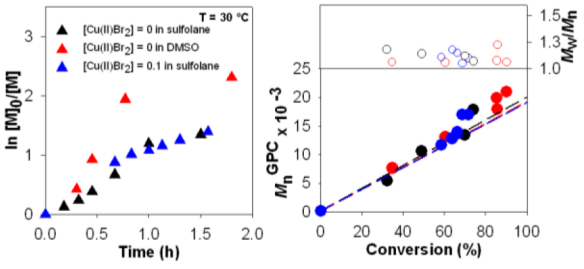

Figure 1. Kinetic plots of conversion and $\ln[M]_0/[M]$ vs time (left) and plot of number-average molecular weights (M_n^{GPC}) and $Đ$ (M_w/M_n) vs conversion (right) for the SARA ATRP of MA catalyzed by Cu(0) wire/Cu(II)Br_2/Me_6TREN in sulfolane (black and blue symbols) or DMSO (red symbols) at 30 °C. Conditions: $[MA]_0$/[solvent] = 2/1 (v/v); $[MA]_0$/$[EBiB]_0$/Cu(0) wire/$[Cu(II)Br_2]$/$[Me_6TREN]_0$ = 222/1/Cu(0) wire/0 or 0.1/1.1 (molar); Cu (0): d = 1 mm, l = 5 cm.

affording the synthesis of PMA with very low $Đ$ (~1.05). The conversions reached are very high and the polymerization kinetics are of first-order with respect to monomer conversions.

The influence of the target DP was investigated (Table S1, entries 2–4). It is remarkable to note that even for DP = 1100, the $Đ$ value of PMA is very low (1.04). This low value indicates clearly that in the system reported herein, the contribution of side the reactions is minimal.

The reduction of Cu(II)Br_2/Me_6TREN by Cu(0) is known to be an important factor in the reaction kinetics.[2] The study of this process in sulfolane and DMSO by UV–vis spectroscopy (Figure S1) reveals no major differences in between both solvents.

The use of sulfolane as solvent was extended to the SARA ATRP of MMA, St, and VC (Table S1, entries 5–16, and Figure 2). The necessary adjustments in the polymerization

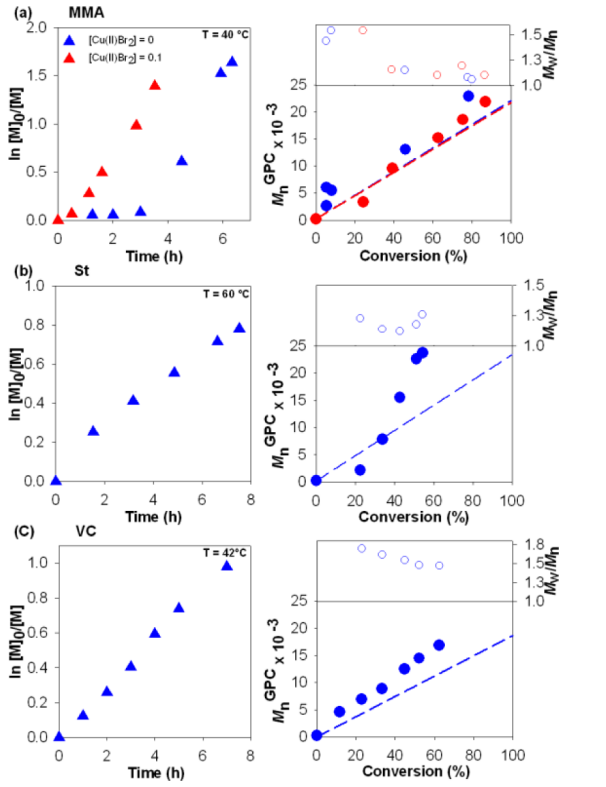

Figure 2. Kinetic plots of conversion and $\ln[M]_0/[M]$ vs time and plot of number-average molecular weights (M_n^{GPC}) and $Đ$ (M_w/M_n) vs conversion for the SARA ATRP of (a) MMA, (b) St, and (c) VC using Cu(0) wire as a supplemental activator and reducing agent in sulfolane. Conditions: (a) $[MMA]_0$/$[EBPA]_0$/Cu(0) wire/$[Cu(II)Br_2]_0$/$[bpy]_0$ = 222/1/Cu(0) wire/0 (blue) or 0.1 (red)/2.2 (molar), $[MMA]_0$/[Sulfolane] = 1/1 (v/v) and T = 40 °C; (b) $[St]_0$/$[EBiB]_0$/Cu(0) wire/$[PMDETA]_0$ = 222/1/Cu(0) wire/1.1 (molar), $[St]_0$/[Sulfolane] = 2/1 (v/v) and T = 60 °C; (c) $[VC]_0$/$[CHBr_3]_0$/Cu(0) wire$]_0$/$[TREN]_0$ = 222/1/Cu(0) wire/1.1, $[VC]_0$/[Sulfolane] = 1/1 and T = 42 °C; Cu(0): d = 1 mm, l = 5 cm.

conditions were done regarding the initiator, ligand, ratio monomer/sulfolane, and temperature taking into account the structure of each monomer.[6,15,20] Figure 2 demonstrates the possibility of synthesizing poly(methyl methacrylate) (PMMA), PS, and PVC with controlled molecular weights by SARA ATRP in sulfolane. The rate of polymerization is of first-order with respect to the monomer conversion, and the final $Đ$ of the

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polymers is similar to the best values reported in the literature[6,15,20] for different monomers. In the case of MMA polymerization, the induction period observed (Figure 2a) was eliminated by adding Cu(II)Br_2 in the beginning of the polymerization, in accordance with the previous results reported by our research group.[6]

The kinetic data obtained for the different monomers is particularly relevant for St (Figures 2b and Figure S2 and Table S1, entries 10−13). Different issues hamper its controlled synthesis, such as low propagation rate compared to acrylates, thermal self-initiation, occurrence of irreversible termination reactions, vitrification, and poor solubility of most catalysts.[9] The results presented herein report the synthesis of PS under mild reaction conditions using a common solvent applied to other monomer families, which opens a portfolio of opportunities for the straightforward synthesis of block copolymers using PS segments.[9]

The structure of the obtained polymers was assessed by ^{1}H NMR and MALDI-TOF analysis (Figure S3 - S8). The "living" nature of the polymer chain-ends was confirmed by carrying out successful chain extension experiments using PMA, PMMA, and PS macroinitiators (Figures S9−S11). As a proof-of-concept, macroinitiators of α,ω-di(bromo)PVC were used to afford block copolymers of PMA-*b*-PVC-*b*-PMA and PS-*b*-PVC-*b*-PS using Me_6TREN and PMDETA as ligands, respectively (Figure 3). Figure 3 shows the movement of the

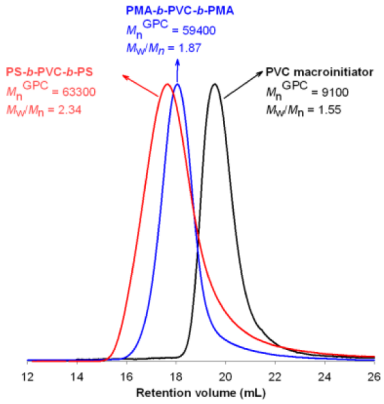

Figure 3. GPC traces of the Br-PVC-Br ($conv_{VC}$ = 48.4%, M_n^{th} = 5500, M_n^{GPC} = 9100, $Đ$ = 1.55) macroinitiator (black line), and the PMA-*b*-PVC-*b*-PMA ($conv_{MA}$ = 86.5%, M_n^{th} = 53800, M_n^{GPC} = 59400, $Đ$ = 1.87) (blue line) and PS-*b*-PVC-*b*-PS ($conv_{St}$ = 57.5%, M_n^{th} = 45000, M_n^{GPC} = 63300, $Đ$ = 2.34) block copolymers (red line).

low molecular weight PVC GPC trace ($conv_{VC}$ = 48.4%, M_n^{th} = 5500, M_n^{GPC} = 9100, $Đ$ = 1.55) toward high molar mass PMA-*b*-PVC-*b*-PMA ($conv_{MA}$ = 86.5%, M_n^{th} = 53800, M_n^{GPC} = 59400, $Đ$ = 1.87) and PS-*b*-PVC-*b*-PS ($conv_{St}$ = 57.5%, M_n^{th} = 45000, M_n^{GPC} = 63300, $Đ$ = 2.34) block copolymers. Nevertheless, the movement is not complete either because the system is not optimized or due to the previously mentioned issues regarding the RDRP of styrene. The structure of the block copolymers was confirmed by ^{1}H NMR (Figures S12 and S13). These results prove the "living" character of the PVC and the possibility of using the reported system in the synthesis of unique block copolymers. It should be mentioned that, to the best of our knowledge, the preparation of block copolymers containing PVC and PS blocks by sequential addition of the appropriated monomers by any RDRP method has never been reported.

In an attempt to push the potential of the system, the PMA-*b*-PVC-*b*-PMA was synthesized using the "one-pot" chain extension approach (Figure 4).

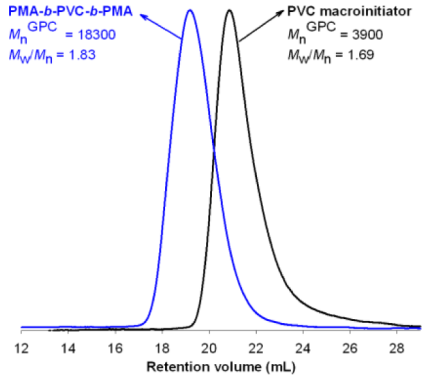

Figure 4. GPC traces of the Br-PVC-Br ($conv_{VC}$ = 62.2%, M_n^{th} = 3000, M_n^{GPC} = 3900, $Đ$ = 1.69) macroinitiator (right curve), and the PMA-*b*-PVC-*b*-PMA ($conv_{MA}$ = 85.7%, M_n^{th} = 17800, M_n^{GPC} = 18300, $Đ$ = 1.83) block copolymer (left curve) prepared by "one-pot" SARA ATRP chain extension.

The GPC traces presented in Figure 4 proves the remarkable advantage of using a single solvent to afford the controlled polymerization of different families of monomers. By using a straightforward procedure involving no purification steps, it is possible to afford well-controlled polymeric structures. The results summarized in Table S1 demonstrate that by adjusting the catalytic complexes and the initiator it is possible to afford a controlled polymerization of MA, MMA, St and VC by SARA ATRP in sulfolane. The presented values regarding k_p^{app}, conversion and $Đ$ are in agreement with the best results reported in the literature for each monomer individually.[6,15,20]

In conclusion, the results presented herein establish an innovative and robust system to assess a vast portfolio of well-defined polymers and block copolymers using a common industrial solvent, and employing at the same time low amounts of soluble copper catalyst.

■ ASSOCIATED CONTENT

Supporting Information

Materials, techniques, procedures, kinetic data, ^{1}H NMR spectra, MALDI-TOF data, and UV−vis spectroscopic study of the catalytic systems. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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