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Photoinduced Metal-Free Atom Transfer Radical Polymerization of Acrylonitrile

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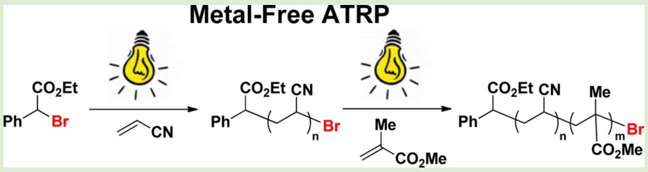
Supporting Information

ABSTRACT: Photoinduced metal-free atom transfer radical polymerization has been successfully extended to the synthesis of polyacrylonitrile (PAN) with predictable molecular weights and low dispersities. This was achieved using phenothiazine derivatives as photoredox catalysts, which activate dormant alkyl bromides to reversibly form propagating radicals. Both ^1H NMR spectroscopy and chain-end extension polymerization show highly preserved Br chain-end functionality in the synthesized PAN.

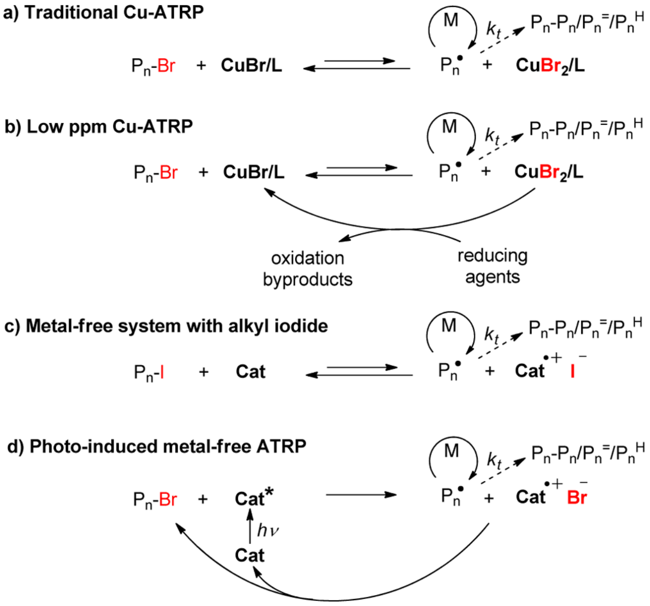


Atom transfer radical polymerization (ATRP)[1] is among the most efficient reversible deactivation radical polymerization systems (RDRP, also termed controlled radical polymerization, CRP).[2] Other successful RDRP systems include nitroxide-mediated polymerization,[3] organometallic radical polymerization,[4] and reversible addition–fragmentation chain transfer systems.[5] ATRP and other RDRP techniques provide new avenues for the preparation of polymers with precisely controlled architecture[6] from a large range of functional monomers.

Originally, ATRP was carried out with relatively high concentrations (ca. 1000 to 10000 ppm) of Cu-based catalyst in order to compensate for unavoidable radical termination reactions. Radical termination irreversibly oxidizes Cu^I species, used to intermittently activate dormant species, to the Cu^{II} species, that deactivates the propagating radicals and acts as the persistent radical.[7] However, at high $[Cu^{II}]/[Cu^I]$ ratio, polymerization ceases and the reaction stops (Scheme 1a). Recently, several systems were developed that enabled ATRP to proceed at a catalyst loading of only 10–100 ppm of Cu.[8] This occurs in the presence of various reducing agents that continuously regenerate Cu^I activators from Cu^{II} deactivators and compensates for radical termination (Scheme 1b). Reducing agents employed in activator regeneration by electron transfer (ARGET) ATRP include various organic reducing agents, such as ascorbic acid[9] and sugars,[10] or inorganic species such as tin(II) complexes,[11] sulfites,[12] metals,[13] or hydrazine.[14] Some reducing agents can also react directly with alkyl halides as supplemental activators and reducing agents, as in (SARA) ATRP[15] (also called SET-LRP).[16] One can also use conventional radical initiators for the same purpose, as in initiators for continuous activator regeneration (ICAR) ATRP.[14] In addition, nonchemical methods employing electrochemical mediation (*e*ATRP)[17] or light (photoATRP)[18] have been developed. In all of these systems, the concentration of Cu catalyst can be reduced below 100 ppm. Such a low level of catalyst can remain in the products for less demanding applications or can be removed by dialysis, precipitation, or filtration.[19] Also, catalysts could be immobilized or reclaimed using various techniques.[20]

Nevertheless, it would be very desirable to develop an ATRP method that does not use transition metals catalysts, especially for some electronic or biomaterials applications. Systems based on alkyl iodides and various organic catalysts were previously

Scheme 1. ATRP Equilibria in (a) Traditional Cu-Based System, (b) Low ppm of Cu System, (c) Metal-Free System with Alkyl Iodides, and (d) Photoinduced Photoredox System with Alkyl Bromides[a]



[a] M, monomer; P_n-P_n/$P_n^=$/P_n^H, terminated polymer chains.

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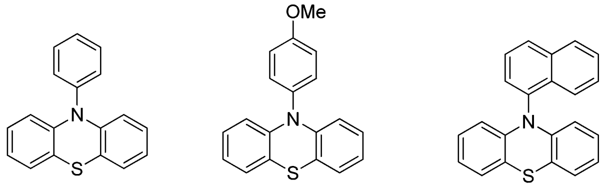
described (Scheme 1c).[21] However, they rely on the much weaker C−I bond and the ability of iodine to form various hypervalent species. It remains a challenge to extend such metal-free catalytic systems to alkyl bromides, commonly used in ATRP. Very recently, Hawker reported a photoinduced metal-free ATRP of methyl methacrylate using 10-phenylphenothiazine (Ph-PTZ) as an organic photocatalyst.[22] In this photoinduced, metal-free ATRP mechanism, a three component photoredox cycle is conducted. The photoexcited PTZ* activates an alkyl halide and generates radicals, while the $PTZ^{+\bullet}Br^{-}$ specie deactivates the radical and regenerates the ground state PTZ (Scheme 1d). Perylene was also used as a successful photocatalyst for metal-free ATRP.[23]

In this communication we report that Ph-PTZ and other phenothiazine derivatives, such as 10-(4-methoxyphenyl)-phenothiazine (4-MeOPh-PTZ) and 10-(1-naphthalenyl)-phenothiazine (Nap-PTZ), can be used as organic photocatalysts for ATRP of acrylonitrile[24] (Figure 1). Acrylonitrile-based block copolymers have been recently used as precursors for N-doped nanostructured carbons.[25] Such materials show interesting catalytic properties and excellent performance as supercapacitors, materials for CO_2 capture, catalysts for oxygen reduction or counter electrodes in dye sensitized solar cells.[26] Since residual amounts of Cu could potentially impact the properties of the nanostructured carbons, it is interesting to evaluate properties of nanostructured carbons prepared in the absence of any transition metal catalysts. However, this paper is focused only on the synthetic aspects of metal-free ATRP of acrylonitrile and block copolymers, while the preparation and performance of new N-doped nanostructured carbons will be presented elsewhere.



Ph-PTZ, **1** 4-MeOPh-PTZ, **2** Nap-PTZ, **3**

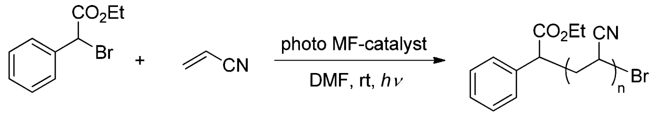
Figure 1. Structures of phenothiazine derivatives used as photocatalysts in metal-free ATRP.

A typical experimental procedure for synthesis of PAN by photoinduced metal-free ATRP follows: 1.3 mL of acrylonitrile (AN, 1.05 g, 20 mmol, 100 equiv), 0.035 mL of ethyl α-bromophenylacetate (EBPA, 48.6 mg, 0.2 mmol, 1 equiv), 5.5 mg of Ph-PTZ (**1**, 0.02 mmol, 0.1 equiv), and 2.6 mL of DMF were added to a 10 mL Schlenk flask. The flask was tightly sealed and oxygen was removed by three freeze−pump−thaw cycles. The reaction mixture was irradiated by exposure to 2.1 mW/cm^2 UV light. Samples were periodically removed from the reaction mixture by syringe to obtain the conversion of AN by ^1H NMR, and number-average molecular weight M_n, and dispersity (M_w/M_n) by GPC using linear PMMA standards in DMF as the eluent. The final polymer was precipitated by addition of the solution to methanol to provide PAN as a white powder. The precipitated PAN was used for M_n determination by ^1H NMR in DMSO-d_6.

Table 1 summarizes the reaction conditions, conversions, M_n, and M_w/M_n data for metal-free ATRP of acrylonitrile. Using EBPA as ATRP initiator, polymerizations of AN with photocatalysts **1** in DMF provided well-defined PAN (entry 1). Since the molecular weights obtained from DMF GPC using linear PMMA or polystyrene standards are usually overestimated,[27] ^1H NMR of the precipitated PAN was used to calculate the absolute number-average molecular weights (vide infra). Values were similar to the theoretical molecular weights and $M_{n,GPC}$ based on PMMA standards were about 3 times larger than those calculated from NMR. Therefore, in the following discussion, $M_{n,GPC}/3$ values were used, as plotted in Figure 2b.

Figure 2a illustrates the kinetic plots ($\ln[M]_0/[M]$ vs time), and Figure 2b displays the evolution of M_n and M_w/M_n with conversion. The linear semilogarithmic plots suggested that the concentration of the propagating radicals was almost constant

Table 1. Results of Photoinduced Metal-Free ATRP of Acrylonitrile[a]



entry	catalyst	$[AN]_0/[EBPA]_0/[Cat]_0$	time (h)	conversion[b] (%)	$M_{n,th}$[c]	$M_{n,NMR}$[d]	$M_{n,GPC}$[e]	M_w/M_n[e]
1	**1**	100:1:0.1	6	34	2040	1990	6200	1.60
2	**1**	100:0.5:0.05	6	36	4060	4160	13400	1.85
3	**1**	100:2:0.2	6	40	1300	1890	5670	1.63
4	**1**	100:1:0.05	6	23	1460	1730	5450	1.88
5	**1**	100:1:0.2	6	31	1890	1670	5440	1.57
6	**2**	100:1:0.1	6	33	1990	2470	7490	1.69
7	**3**	100:1:0.1	15	42	2470	2630	8140	1.62
8	**1**	100:1[h]:0.1	14	56	3210	4240	13800	1.52
9[f]	**1**	100:1:0.1	7	63	3580	4400	12100	1.42
10[f,g]	**1**	100:1:0.1	7	72	4060	4060	13600	1.53

[a] Reaction conditions: EBPA (1 equiv), AN (50, 100, or 200 equiv), photo MF-catalyst (**1**, **2**, or **3** at 0.05, 0.1, or 0.2 equiv), $[AN]_0$= 5 M, AN/DMF = 1:2 (v/v), at room temperature irradiation by 2.1 mW/cm^2 UV light, M_n = number-average molecular weight, and M_w = weight-average molecular weight. [b] Determined by ^1H NMR. [c] Calculated based on conversion obtained by ^1H NMR (i.e., $M_{n,th} = M_{EBPA} + [AN]_0/[EBPA]_0 \times \text{conversion} \times M_{AN}$). [d] Determined by ^1H NMR of precipitated PAN by comparison the integration of $C\mathbf{H}CNBr$ with $C\mathbf{H}_2C\mathbf{H}CN$ (i.e., DP = 1/3 area($C\mathbf{H}_2C\mathbf{H}CN$)/area($C\mathbf{H}CNBr$); $M_{n,NMR} = M_{EBPA} + DP \times M_{AN}$). [e] Determined by GPC in DMF, based on linear PMMA as calibration standards. [f] Irradiation by 4.9 mW/cm^2 UV light. [g] In DMSO. [h] BPN instead of EBPA.

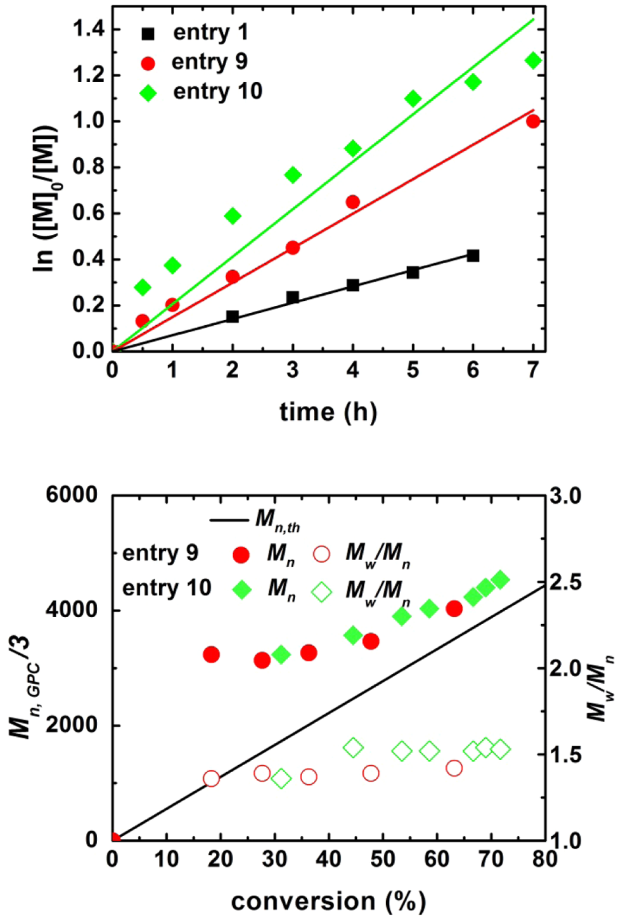


Figure 2. (a) Semilogarithmic kinetic plots of polymerization of AN with photoinduced metal-free ATRP methods under conditions [AN]:[EBPA]:[1] = 100:1:0.1 in DMF or DMSO, irradiation by 2.1 or 4.9 mW/cm^2 UV light; (b) number-average molecular weight (M_n, filled symbols) and dispersity (M_w/M_n, open symbols) vs conversion for metal-free ATRP of AN.

throughout the polymerization. With a stronger UV source (entry 10) the rate decreased with conversion. Molecular weights seem to follow theoretical values after about 50% conversion suggesting the complete initiation. Values of M_w/M_n about 1.5 can indicate relatively slow deactivation caused by either low deactivator concentration or low values of deactivation rate constants.

Entries 2 and 3 in Table 1 show the results from the photoinduced metal-free ATRP of AN targeting two different DPs (200 and 50). For DP = 200, the $M_{n,NMR}$ was close to the $M_{n,th}$, values predicted by the ^{1}H NMR conversion (i.e., $M_{n,th}$ = M_{EBPA} + DP × conv. × M_{AN} = 243 + DP × conv. × 53), but dispersity was large (M_w/M_n = 1.85) probably due to the low concentration of catalyst. For DP = 50, the molecular weight was slightly higher than the theoretical value, indicating low initiation efficiency. The polymerization targeting DP = 50 was slightly faster (see Figure S1) because of higher concentrations of initiator and catalyst, as compared to entry 1 (i.e., for DP = 50, $[EBPA]_0$ = 0.1 M, $[Cat]_0$ = 0.01 M; for DP = 100, $[EBPA]_0$ = 0.05 M, $[Cat]_0$ = 0.005 M).

The polymerizations of AN with different concentrations of photocatalyst were also investigated with conditions [AN]/[EBPA]/[**1**] = 100:1:0.05 where $[\mathbf{1}]_0$ = 0.0025 M. The obtained PAN had slightly higher M_w/M_n than previously obtained (cf. entry 4 vs 1). The first-order kinetic plot for this reaction showed a downward curvature (see Figure S2), suggesting termination reactions occurred with this low catalyst loading. The metal-free ATRP of AN with $[\mathbf{1}]_0$ = 0.01 M provided PAN with better control (M_w/M_n = 1.57, cf. entry 5 vs 1).

It is interesting to note that while phenothiazines are powerful inhibitors used for storage of acrylic acid,[28] they can also act as photocatalysts due to their strongly negative redox potential in the excited state.[22] There is also possibility for hydrogen abstraction by $PTZ^{+\bullet}Br^-$, as reported in cationic polymerization.[29] Hence, two additional phenothiazines derivatives **2** and **3** were investigated and both successfully provided well-defined PAN in metal-free ATRP reactions (entries 6 and 7). An induction period (around 1 h) was observed for Nap-PTZ catalyzed polymerization of AN (see Figure S3).

2-Bromopropionitrile (BPN), a widely used initiator for ATRP of AN,[24,27] was tested instead of EBPA in the metal-free ATRP of AN (entry 8). The molecular weights increased with conversion at the beginning of polymerization, but they were higher than the theoretical values, suggesting that the initiator was not completely consumed and that the more active EBPA is a more efficient initiator for metal-free ATRP.

A stronger UV light source (4.9 mW/cm^2) was also used in metal-free ATRP of AN under similar polymerization conditions [AN]/[EBPA]/[**1**] = 100:1:0.1 in DMF and provided PAN with better control (M_w/M_n = 1.42, entry 9). The kinetic plot showed that the polymerization under a stronger light source (4.9 vs 2.1 mW/cm^2) was faster (entries 9 vs 1). Since DMSO is also a suitable solvent for PAN, the polymerization of AN was investigated in DMSO (entry 10). The polymerization in DMSO was faster than in DMF and provided PAN with predicted M_n and a dispersity of 1.53. For both entries, 9 and 10, the M_n increased with conversion, but M_n was higher than theoretical values of M_n at the beginning of the polymerization (Figure 2b), which indicates slow initiation.

Figure 3 shows the ^{1}H NMR spectrum of PAN in DMSO-d_6, obtained from the photoinduced metal-free ATRP under the conditions where [AN]/[EBPA]/[**1**] = 100:1:1 in DMF (entry 1). Both the ethyl phenylacetate and bromine end groups are observed. The aromatic protons H_a (7.35 ppm), ethyl groups H_b (1.14 ppm), H_c (4.09 ppm), and H_d (3.83 ppm) are from the initiator, and the proton at 5.1−5.3 ppm is from the growing end group $CHBr(CN)$. The backbone of PAN consists of two types of protons: CH_2CHCN (H_e, 2.05 ppm) and CH_2CHCN (H_f, 3.16 ppm). The molecular weight $M_{n,NMR}$ was

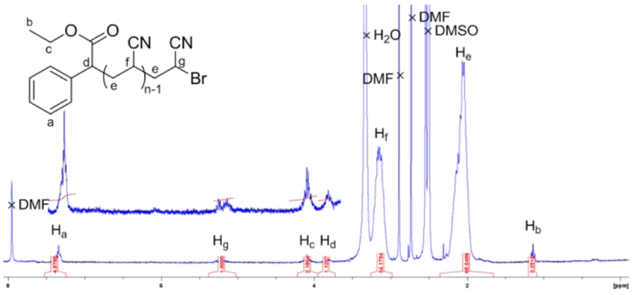
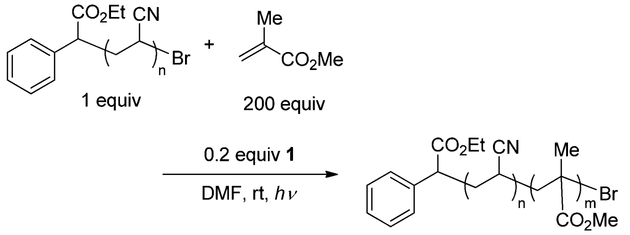


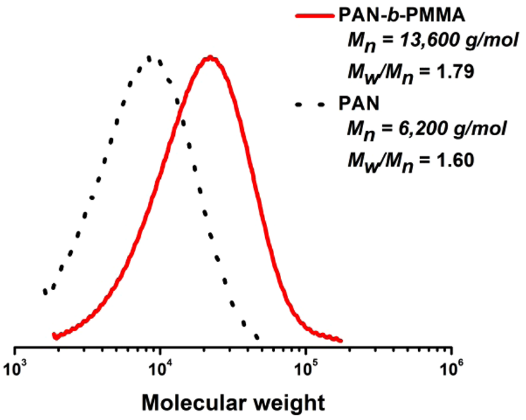
Figure 3. ^{1}H NMR spectrum of PAN in DMSO-d_6, obtained from photoinduced metal-free ATRP under conditions [AN]/[EBPA]/[**1**] = 100:1:0.1 in DMF.

calculated by comparison of the area of the peaks of H_g from the end group with H_e and H_f from the polymer backbone (i.e., DP = [area(H_e) + area (H_f)]/3/area(H_g); $M_{n,NMR} = M_{EBPA} + DP \times M_{AN}$; cf. Supporting Information).

To confirm the utility of this photoinduced metal-free ATRP method, chain extension of the homopolymer PAN ($M_{n,GPC}$ = 6200, M_w/M_n = 1.60) was investigated. Chain extension of macroinitiator PAN-Br with MMA was conducted with 0.2 equiv **1** at rt with UV irradiation for 15 h, providing a well-defined PAN-*b*-PMMA block copolymer ($M_{n,GPC}$ = 13600, M_w/M_n = 1.79, Scheme 2). The GPC trace clearly shifted to a higher molecular, which suggests that the synthesized PAN had excellent bromine chain-end functionality and high efficiency for crosspropagation. To further confirm this result, the PAN-*b*-PMMA copolymer was isolated via precipitation in methanol, and the ^{1}H NMR of the copolymer in DMSO-d_6 was recorded (Figure 4). Two types of methyl protons H_h and H_i at 3.57 and 0.58−1.09 ppm, as well as the CH_2 protons (H_g, 1.30−1.96 ppm) from MMA backbone were observed. The ethyl phenylacetate group from the initiator and the protons from PAN were also clearly preserved. A comparison of the area of the protons from PAN with the protons from PMMA, was used to calculate the DP of PMMA as 103, which is in agreement with 52% conversion of MMA by ^{1}H NMR in the chain extension reaction (see Figure S7).

Scheme 2. Chain Extension of PAN with MMA by Photoinduced Metal-Free ATRP





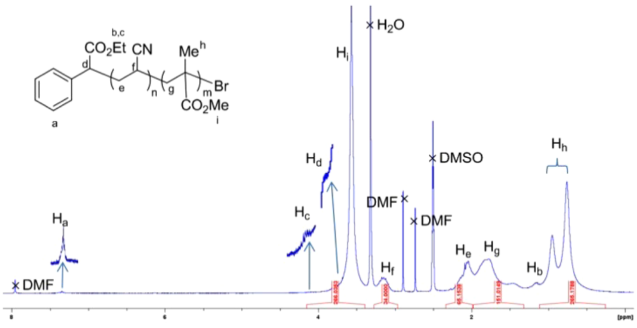


Figure 4. ^{1}H NMR spectrum of PAN-*b*-PMMA in DMSO-d_6, obtained from photoinduced metal-free ATRP under conditions [PAN-Br]/[MMA]/[1] = 1:200:0.2, MMA/DMF = 1:2 (v/v) at rt and irradiation by 2.1 mW/cm^2 UV light.

In conclusion, three phenothiazine derivatives were evaluated as catalysts for photoinduced metal-free ATRP of acrylonitrile. Both NMR and chain-extension polymerization confirm that the synthesized PANs have highly preserved bromine chain-end functionality, which supports the ATRP mechanism. This metal-free ATRP method could be useful for the synthesis of electronic materials without residual transitional metal. However, when compared to traditional Cu-based ATRP, this metal-free method still has room for further improvement; such as enhancing initiator efficiency, generating polymers with higher molecular weight, and lower dispersity.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures for preparation and characterization of all compounds. 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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