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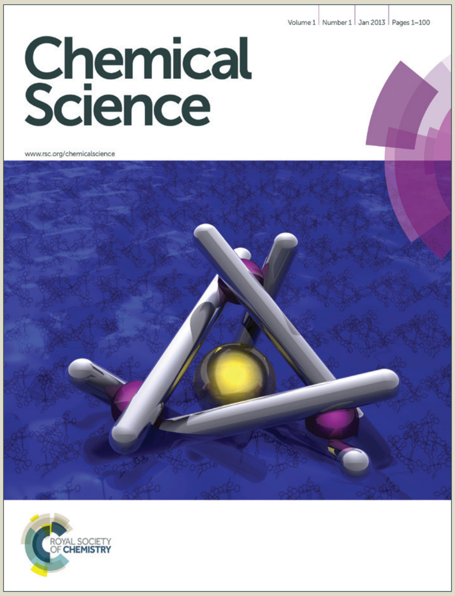

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Employing Exchange Reactions Involving Hypervalent Iodine Compounds for the Direct Synthesis of Azide-Containing Linear and Branched Polymers

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Abstract

A method for the preparation of azide-containing linear and branched polymers was developed that takes advantage of the efficient exchange of the acetoxy "ligands" in (diacetoxyiodo)benzene $PhI(O_2CCH_3)_2$ (Ph = phenyl) with azides, for instance in the presence of sodium azide. The *in-situ* generated azide-containing hypervalent iodine(III) compounds $PhI(O_2CCH_3)N_3$ and $PhI(N_3)_2$ decomposed rapidly, even at temperatures close to the ambient, to the monovalent iodine compound (iodobenzene) and azide (and – in the former case – also acetoxy and/or methyl) radicals. The reactive azide radicals initiated the polymerization of methyl methacrylate at 40-100 ^{o}C, yielding polymers with an azide functionality at the α-terminus. Fast termination by coupling of the propagating radicals with azide radicals and possibly azide transfer from $PhI(N_3)_x(O_2CCH_3)_{2-x}$ (x = 1, 2) were responsible for the formation of low-molecular-weight linear polymers with an azide group at the ω-end. When the polymerizations were carried out in the presence of divinyl compounds (crosslinkers), highly branched polymers were produced prior to gelation. The network formation was delayed in these systems until moderate to high monomer conversions were reached due to the aforementioned termination and/or transfer, which limited the size of the interconnected chains and therefore the average number of incorporated pendant vinyl groups per chain. The use of the $PhI(O_2CCH_3)_2$ – NaN_3 initiating system proved to be an efficient one-pot route to mono- and diazide-capped linear or multi-azidated branched polymers that could be easily functionalized, e.g., under azide-alkyne "click" coupling conditions with alkynes, such as propargyl 4-(1-pyrenyl)butyrate.

Keywords: branched polymers, hypervalent iodine compounds, azides, azide radicals, "click" chemistry, one-pot synthesis

Introduction

The organic compounds of hypervalent iodine were first described at the close of the XIXth century, including those containing iodine(III), such as (dichloroiodo)arenes ($ArICl_2$; Ar = aryl),[1] iodosylarenes (ArIO),[2,3] (diacyloxyiodo)arenes ($ArI(O_2CR)_2$),[3] and diaryliodonium salts ($Ar_2I^+A^-$; A^- is an anion),[4,5] or iodine(V), such as iodylarenes ($ArIO_2$).[3] Since then, a great variety of hypervalent iodine compounds have been discovered, and numerous review articles[6-14] and monographs[15-17] deal with their synthesis, characterization, reactivity, and uses. According to the now-classical description,[18] hypervalent molecules contain 3-center-4-electron bonds, which are longer and weaker than the traditional 2-center-2-electron bonds and can be easily cleaved either hetero- or homolytically with the formation of ions or radicals, respectively. The "ligands" L in $ArIL_2$ (e.g., L = Cl, RCO_2) can exchange with nucleophiles (Nu^-) to afford new hypervalent iodine compounds, first ArI(L)Nu and eventually $ArINu_2$, the hypervalent I-Nu bonds of which can in turn dissociate homolytically and yield iodoarene and the radicals $Nu^\bullet$. Thus, ligand exchange followed by photo- or thermolysis of the reaction products is a convenient way to convert various nucleophiles into radicals, which can participate in numerous useful organic transformations.[9-14]

Because hypervalent iodine compounds can participate in ionic and/or radical,[19,20] as well as in "ligand" exchange[12] reactions, they have attracted the attention of synthetic polymer chemists. For instance, upon photolysis iodonium salts generate cationic species and are thus useful as initiators of cationic polymerization of vinyl and heterocyclic monomers.[21,22] The hypervalent I-O bonds in $ArI(O_2CR)_2$ can be cleaved homolytically upon either irradiation or heating, and the generated acyloxy radicals ($RCO_2^\bullet$) or the products of their decarboxylation ($R^\bullet$), initiate radical polymerization.[23-25]

(Hyper)branched polymers[26-29] are of significant interest due to applications in diverse fields, and a number of procedures for their synthesis have been developed, including both step- and chain-growth polymerizations. One of the popular chain-growth methods, named "self-condensing vinyl polymerization", involves the homo- or copolymerization of compounds that contain both polymerizable and initiating groups (inimers).[30,31] A drawback of the method is that it often requires multi-step synthesis of inimers. However, it was recently reported that inimer molecules could be formed *in situ* through a "ligand" exchange reaction between hypervalent iodine(III) compounds, such as (diacetoxyiodo)benzene $PhI(O_2CCH_3)_2$ (Ph = phenyl), DAIB, and carboxylate-containing monomers, such as methacrylic acid.[32] The other important chain-growth techniques affording hyperbranched polymers are based on the radical copolymerization of mono- and di- or multivinyl monomers (crosslinkers) in the presence of reagents able to limit the size of the polymer chains and therefore the number of incorporated pendant vinyl groups per macromolecule. As a result, the gelation point is delayed and hyperbranched polymers are formed up to relatively high monomer conversions. Additives that have been successfully employed include chain transfer agents[33-40] and reagents capable of reversibly deactivating the propagating radicals.[41,42] The molecular weight can also be limited by increasing the rate of termination, i.e., by generating a high concentration of radicals. To achieve that, substantial amounts of radical sources (initiators) are added to the reaction mixture and the reaction is carried out at conditions at which their decomposition is fast.[43-45] This approach has not been studied extensively, mostly due to the difficulties associated with controlling the decomposition rate of large amounts of radical precursors, which can be especially problematic on a large scale. However, the procedure is valuable when functional radicals are used to initiate the polymerization and to combine with the propagating radicals because it provides an easy one-pot access to functionalized (hyper)branched macromolecules.

The azide radical[46,47] is a particularly interesting functional radical because it can initiate the polymerization of vinyl monomers,[48-52] yielding azide-capped polymers, and can serve as a precursor of numerous organic azides, which are attractive because of their ability to undergo a vast range of chemical transformations,[53-58] including azide-alkyne (“click”) cycloadditions.[59-67] Azide radicals can be generated either in homogeneous systems or electrochemically (on the surface of an electrode[68,69]) via oxidation of azide anions. An alternative approach is to react hypervalent iodine(III) compounds of the type $ArIL_2$ (L = Cl, RCO_2) or ArIO with an azide source such as NaN_3 or $(CH_3)_3SiN_3$. Under these conditions, a mixture is produced consisting of the unstable compounds $ArI(N_3)L$ and $ArI(N_3)_2$, which decompose rapidly to iodoarene and azide radicals (and, in the former case, also the radicals $L^{\bullet}$). This methodology has been successfully applied for the azidation of various substrates.[70]

In this work, the utility is demonstrated of the compounds $PhI(N_3)_x(O_2CCH_3)_{2-x}$ (x = 1, 2) generated *in situ* from DAIB and NaN_3 as sources of azide radicals, which could both initiate polymerization and participate in bimolecular termination reactions with the propagating radicals. When copolymerization of monovinyl monomers and divinyl crosslinkers is carried out in the presence of the DAIB – NaN_3 system, multiazidated highly branched polymers are formed due to the delayed gelation in the presence of large concentration of azide radicals and/or due to the ability of $PhI(N_3)_x(O_2CCH_3)_{2-x}$ (x = 1, 2) to transfer azide groups to the growing chains.

Experimental

Materials

Methyl methacrylate (MMA, 99%, Acros), ethylene glycol dimethacrylate (EGDMA, Alfa Aesar, 98%), propargyl alcohol (99%, Acros), 4-(1-pyrenyl)butyric acid (97%, Acros), NaN_3 (99%, EMD Millipore), DAIB (98%, Aldrich), *N*,*N*-dicyclohexylcarbodiimide (DCC, 99%, Aldrich), 4-(dimethylamino)pyridine (4-DMAP, 99%, Aldrich), 2,2,6,6-tetramethylpiperidinyloxyl (TEMPO, 98 %, Acros), *N*,*N*-dimethylformamide (DMF, EMD Milipore, 99.98%), *N*,*N*-dimethylacetamide (DMAc, 99 %, Alfa Aesar), dimethyl sulfoxide (DMSO, 99.9%, BDH), tetrahydrofuran (THF, 99.5 %, EMD Milipore), chloroform (99+%, Acros), chlorobenzene (PhCl, 99%, Acros) were used as received. The deuterated solvent ($CDCl_3$) was a product of Cambridge Isotope Laboratories. A small amount of tetramethylsilane (TMS) was added to as a chemical shift reference.

Analyses

Molecular weights and molecular weight distribution dispersities (M_w/M_n) were determined by size exclusion chromatography (SEC) on a Tosoh EcoSEC system equipped with a series of 4 columns (TSK gel guard Super HZ-L, Super HZM-M, Super HZM-N, and Super HZ2000) and using refractive index (RI) and UV detectors. THF was used as the eluent at a flow rate of 0.35 mL min^{-1} (40 °C). The SEC calibration was based on linear polystyrene standards. To obtain a more reliable molecular weight measurement for one of the linear azide-capped polymers, SEC was employed with calibration based on polyMMA standards, as mentioned in the text. Monomer conversions were determined by NMR spectroscopy using a Bruker Avance DRX DRX (400 MHz) or a JEOL ECCA (500 MHz) spectrometer. Each sample taken from the polymerizing mixtures was added to an NMR tube and diluted with $CDCl_3$ containing TEMPO (to prevent further polymerization) and tetramethylsilane (TMS) as the chemical shift reference. Elemental analyses were carried out at Midwest Microlab, IN. Infrared spectra were collected on a Thermo Scientific Nicolet iS10 FT-IR Spectrometer. The samples were prepared by dissolving 10 mg of polymer in 0.5 mL of THF, followed by casting a film on a NaCl plate. Fluorescence studies were performed using Hitachi F 7000 fluorescence spectrophotometer. The excitation wavelength was λ_{ex} = 340 nm (emission slit = 2.5 nm). Stock polymer solutions (1 mg mL^{-1}) were first prepared in DMF, THF, $CHCl_3$, or DMSO, and were then diluted (0.1 mL into 1 mL of the corresponding solvent), and analyzed. The emission spectrum of propargyl 4-(1-pyrenyl)butyrate in THF (3.33 µg mL^{-1}) was acquired from a solution of the same concentration. Thermo-gravimetric analyses (TGA) were performed on a Perkin-Elmer TGA 4000 thermogravimetric analyzer. The samples (ca. 3 mg) were heated in a ceramic pan from 40 to 500 °C at a rate of 10 °C min^{-1} under nitrogen flow (20 mL min^{-1}).

Synthetic procedures

CAUTION: Azides should be handled with care due to their toxicity and ability to explode when heated or under friction. The reactions involving DAIB and NaN_3 *yield unstable azide-containing hypervalent iodine(III) compounds, which decompose, even at low temperatures, with the formation of azide radicals. The bimolecular combination of azide radicals yields* N_2 *and hydrogen abstraction from the reaction mixture components yields* HN_3*, both of which are gasses and can lead to elevated pressures inside the reaction vessels. It is recommended that the reactions are carried out on a small scale (not significantly exceeding the scale of the following procedures) and that protective equipment is used.*

Linear azide-capped polyMMA. A stock solution of DAIB and MMA was prepared by dissolving DAIB (0.1731 g, 5.37×10^{-4} mol) in a mixture of MMA (1.07 mL, 1.0×10^{-2} mol) and PhCl (7.5 mL) in a round bottom flask equipped with a magnetic stir bar, and sealed with a rubber septum (secured with electric tape), and wrapped with aluminum foil to prevent exposure of the contents to light. The mixture was stirred for 20 min to dissolve DAIB and was then deoxygenated by five freeze-pump-thaw cycles, and back-filled with N_2. In a thick-walled test tube equipped with a magnetic stir bar and wrapped with aluminum foil, NaN_3 was added (0.0650 g, 1.0×10^{-3} mol). The test tube was sealed with a rubber septum and was evacuated and back-filled with N_2 five times to remove air. Then, 8 mL of the stock solution of DAIB was transferred to the tube using a nitrogen-purged syringe. The tube was placed in an oil bath at 100 °C. The amount of NaN_3 in the final reaction mixture was 2 eq vs. DAIB. At timed intervals, samples (ca. 0.04 mL) were withdrawn from the mixture with a nitrogen-purged syringe, part of which were then diluted with $CDCl_3$ (for NMR analysis) and part – with THF (for SEC analysis). To each solvent, a small crystal of TEMPO had been added prior to the sample preparation in order to prevent further polymerization during the analyses. Similar experiments were carried out using different amounts of NaN_3 (0.1300 g (4 eq vs. DAIB) or 0.2600 g (8 eq vs. DAIB)), or with no NaN_3 (control experiment), or using DMAc as the solvent, either at 100 or 40 ^{o}C.

To collect a sufficient amount of polymer for analysis, the reaction carried out in PhCl at 40 ^{o}C with $[NaN_3]_0 : [DAIB]_0 = 8:1$ was scaled up 3-fold. The reaction was stopped at 75 % monomer conversion by opening the flask to air. The reaction mixture was immediately passed through a column containing silica (3-cm layer packed in a 12-mL syringe) to remove unreacted NaN_3 and the formed in the reaction CH_3CO_2Na. The adsorbent in the column was washed with 10 mL of THF and the combined polymer solution was dialyzed against methanol (2 × 2 L) using a dialysis membrane with molecular weight cut-off of 1,000 Da to remove PhCl. The contents of the dialysis tube (heterogeneous due to precipitation of some of the polymer) were transferred into a flask and the methanol was removed on a rotary evaporator at 40 °C. The polymer was re-dissolved in 30 mL of THF and an additional dialysis was carried out against a mixture of water and methanol (1:1 by volume; 4 × 2 L) to remove residual NaN_3. Finally, the methanol and most of the water were removed on a rotary evaporator at 40 °C. The remaining water was removed by freeze-drying. The alternative purification by repeated precipitations of the polymer proved to be inefficient and significant losses of the low-molecular-weight material were observed.

Branched azide-containing polyMMA (b-polyMMA(N_3)$_x$). A stock solution of DAIB, MMA and EGDMA was prepared by dissolving DAIB (0.1731 g, 5.37×10^{-4} mol) in a mixture of MMA (1.07 mL, 1.0×10^{-2} mol), EGDMA (17.7 μL, 9.4×10^{-5} mol) and PhCl (7.5 mL) in a round bottom flask equipped with a magnetic stir bar, and sealed with a rubber septum (secured with electric tape), and wrapped with aluminum foil to prevent exposure of the contents to light. The mixture was stirred for 20 min to dissolve DAIB and was then deoxygenated by five freeze-pump-thaw cycles, and back-filled with N_2. In a test tube equipped with a magnetic stir bar and wrapped with aluminum foil, NaN_3 was added (0.2600 g, 4.0×10^{-3} mol). The test tube was sealed with a rubber septum and was evacuated and back-filled with N_2 five times to remove air. Then, 8 mL of the stock solution of DAIB was transferred to the tube using a nitrogen-purged syringe. The tube was placed in an oil bath at 40 °C. The amount of NaN_3 and EGDMA in the final reaction mixture was 8 eq vs. DAIB and 1 % of MMA, respectively. At timed intervals, samples (0.04 mL) were withdrawn from the mixture with a nitrogen-purged syringe, part of which were then diluted with $CDCl_3$ (for NMR analysis) and part – with THF (for SEC analysis). To both solvents, a small crystal of TEMPO had been added prior to the sample preparation in order to prevent further polymerization. At the end of the reaction, the reaction tube was opened to air to quench polymerization and the final polymer solution was passed through a column filled with silica (ca. 1-cm layer of silica in a 12-mL syringe) to remove the salts. The adsorbent was washed with 10 mL of THF to extract the polymer absorbed by the silica. The final combined polymer solution was precipitated in 250 mL of methanol. The polymer was then re-dissolved in 10 mL of THF and precipitate in a mixture of 100 mL methanol and 25 mL of de-ionized water. The procedure was repeated twice. The polymer was collected by vacuum filtration and dried. Similar experiments were carried out using different amounts of EGDMA 35.4 µL (2 % vs. MMA), 88.5 µL (5 % vs. MMA), 132.8 µL (7.5 % vs. MMA) or 177.0 µL (10 % vs. MMA) using DMAc as the solvent at 40 ^{o}C.

Propargyl 4-(1-pyrenyl)butyrate. 4-(1-pyrenyl)butyric acid (0.8000 g, 2.774×10^{-3} mol), DCC (0.5724 g, 2.774×10^{-3} mol), and 4-DMAP (0.0148 g, 1.206×10^{-4} mol) were weighed in a 25 mL round bottom flask equipped with a stir bar and capped with a rubber septum. THF (10 mL) was injected in the flask, and the contents dissolved within 5 min. Then, propargyl alcohol (120 μL,) was injected and the reaction mixture was stirred at room temperature for 40 h. The solvent (THF) was then evaporated under vacuum and the brown solids were dissolved in 100 mL of cold acetonitrile. The mixture was filtered solution to remove the white solid, and the solvent was removed from the obtained clear solution. The yellow solid material was purified four times by adding cold ether (ca. 15 mL) and filtering off the insoluble material, followed by evaporation of the ether. ^{1}H NMR (500 MHz, $CDCl_3$, δ [ppm]): 8.54 – 7.52 (m, 9H), 4.63 (d, J = 2.3 Hz, 2H), 3.36 – 3.29 (m, 2H), 2.44 (t, J = 7.2 Hz, 2H), 2.42 – 2.36 (m, 1H), 2.15 (dt, J = 14.9, 7.4 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$, δ [ppm]): 172.72 (C=O), 135.60, 131.50, 130.98, 130.11, 128.83, 127.56, 127.53, 127.47, 126.84, 125.94, 125.19, 125.07, 125.03, 124.91, 124.88, and 123.39 (aromatic), 77.80 and 74.95 (C≡C), 52 ($CH{\equiv}C\underline{\mathbf{C}}H_2O$), 33.65 (1-pyrenyl-$\underline{\mathbf{C}}H_2$), 32.76 ($\underline{\mathbf{C}}H_2CO_2$), 26.75 (1-pyrenyl-$CH_2\underline{\mathbf{C}}H_2CH_2CO_2$).

Pyrene-labeled b-polyMMA. B-polyMMA$(N_3)_x$, (0.3360 g, corresponding to ca. 3.84×10^{-5} mol of azide, based on elemental analysis), CuBr (0.0044 g, 1.03×10^{-5} mol), and propargyl 4-(1-pyrenyl)butyrate (0.0524 g, 1.73×10^{-4} mol) were mixed in a tube and a magnetic stir bar was added. The tube was then sealed with a rubber septum, which was secured with electric tape, and the air was removed by applying vacuum and back filling the tube with N_2 five times. DMF purged with N_2 (5 mL) was injected in the reaction vial using a nitrogen-purged syringe. The mixture was stirred at room temperature for 30 h, after which the contents were diluted with ca.

10 mL of acetone. The polymer was precipitated in a mixture containing 45 mL of methanol and 5 mL of water. The liquid was decanted and the polymer was dissolved in 25 mL of acetone. To remove the unreacted propargyl 4-(1-pyrenyl)butyrate, the mixture was dialyzed against acetone (total volume of 2 L) for 5 days, using a regenerated cellulose dialysis membrane with approximate molecular weight cut-off of 2,000 Da. During the procedure, some polymer precipitated; the final product was dried under vacuum and re-dissolved in 20 mL of THF. The polymer was then precipitated in ca. 100 mL of methanol and was then dried in vacuum at room temperature.

Results and discussion

The reaction of DAIB with azide sources such as $(CH_3)_3SiN_3$ at low temperatures (e.g., <10 ^{o}C) yields a mixture of $PhI(N_3)(O_2CCH_3)$ and $PhI(N_3)_2$, as suggested by IR spectroscopic studies.[71] Hypervalent iodine(III) compounds with azide ligand(s) decompose rapidly, even at low temperatures, with the formation of azide radicals – a reaction that has been employed for the azidation of numerous substrates, including alkenes,[72] substituted anisoles,[73,74] buckminsterfullerene,[75] aromatic[76,77] or aliphatic[77] aldehydes, *N,N*-dialkylarylamines,[78] cyclic thioethers,[79] aliphatic hydrocarbons with secondary and tertiary carbon atoms,[80,81] and polymers such as polystyrene.[70] Some of these transformations proceed as radical additions, others – as coupling of azide radicals with carbon-centered radicals derived from the substrate (typically formed after abstraction of a hydrogen atom by an azide radical), and some may proceed via transfer of azide groups from an azide-containing hypervalent iodine(III) compound to a carbon-centered radical.

Synthesis of linear azide-capped polymers. Azide radicals could easily be generated by mixing DAIB with NaN_3, the latter being hydrolytically stable and non-volatile (and therefore less dangerous), as well as less expensive, alternative to $(CH_3)_3SiN_3$. In the presence of MMA, fast polymerizations were observed at 100 ^{o}C, both in relatively non-polar (PhCl) and rather polar solvents (DMAc), as shown in Figure 1.

DAIB itself can serve as a photo-[23] and thermal[24] initiator of polymerization, and in order to assess the effect of NaN_3 on the polymerization kinetics and the molecular weights of the obtained polymers, polymerizations were also conducted using DAIB alone, i.e., in the absence of NaN_3. As seen from Figure 1a and b, the decomposition of DAIB was relatively slow, even at 100 ^{o}C, leading to slow polymerizations. Partially due to the better solubility of DAIB in DMAc, the polymerization in that solvent was somewhat faster (about 26 % monomer conversion in 1 h) than in PhCl (ca. 14 % conversion, also in 1 h). High conversions ($\geq$ 60 %) were eventually reached in both solvents but that took 15 h.

In the presence of NaN_3 (2, 4, or 8 eq vs. DAIB), the polymerizations were markedly faster due to the exchange of acetoxy with azide groups followed by fast decomposition of the newly formed hypervalent iodine(III) compounds ($PhI(N_3)(O_2CCH_3)$ and/or $PhI(N_3)_2$) with formation of azide radicals. Azide radicals are known to add very efficiently to carbon-carbon double bonds, e.g., of 1-octene, 1,3-butadiene, 1,4-diphenyl-1,3-butadiene, or styrene,[68,69] and are efficient polymerization initiators.[48-52] In both solvents the initial polymerization rates increased with the amount of NaN_3 due to the generation of higher concentration of azide radicals. DAIB and NaN_3 are both better soluble in DMAc than in PhCl and as a result, the formation and decomposition of the azide-containing hypervalent iodine(III) compound(s) were faster in the former solvent, particularly at high $[NaN_3]_0$: $[DAIB]_0$ ratios. The rapid decomposition led to fast termination reactions, both involving propagating chains and azide radicals, which caused the polymerizations to stop at moderate conversions. The fast bimolecular termination of azide radicals resulted in the formation of large volumes of N_2. Indeed, the rate coefficients of azide radical termination in aqueous solutions have been reported to be 3 – 4.5×10^9 M^{-1} s^{-1}.[82] As expected, as the concentration of azide radicals increased, i.e., at higher $[NaN_3]_0$: $[DAIB]_0$ ratios or using DMAc as the solvent, the molecular weights of the polymers obtained at the same conversion decreased substantially (Figure 1c and d).

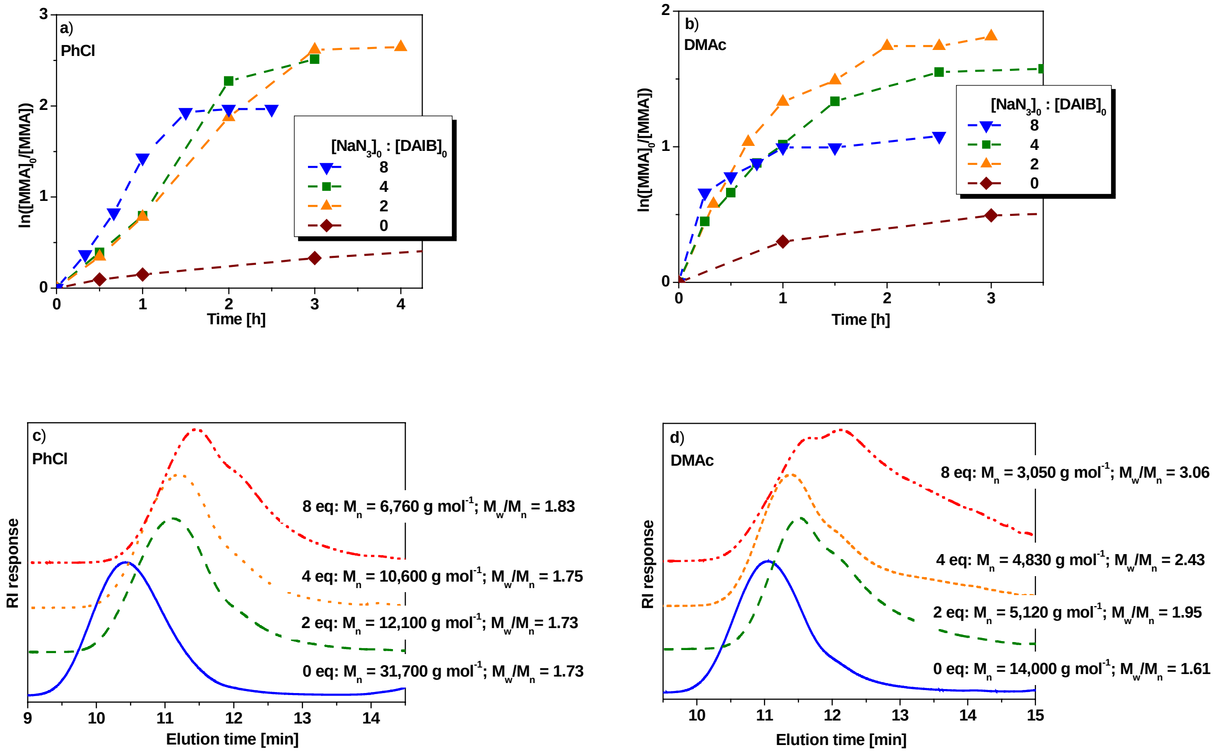
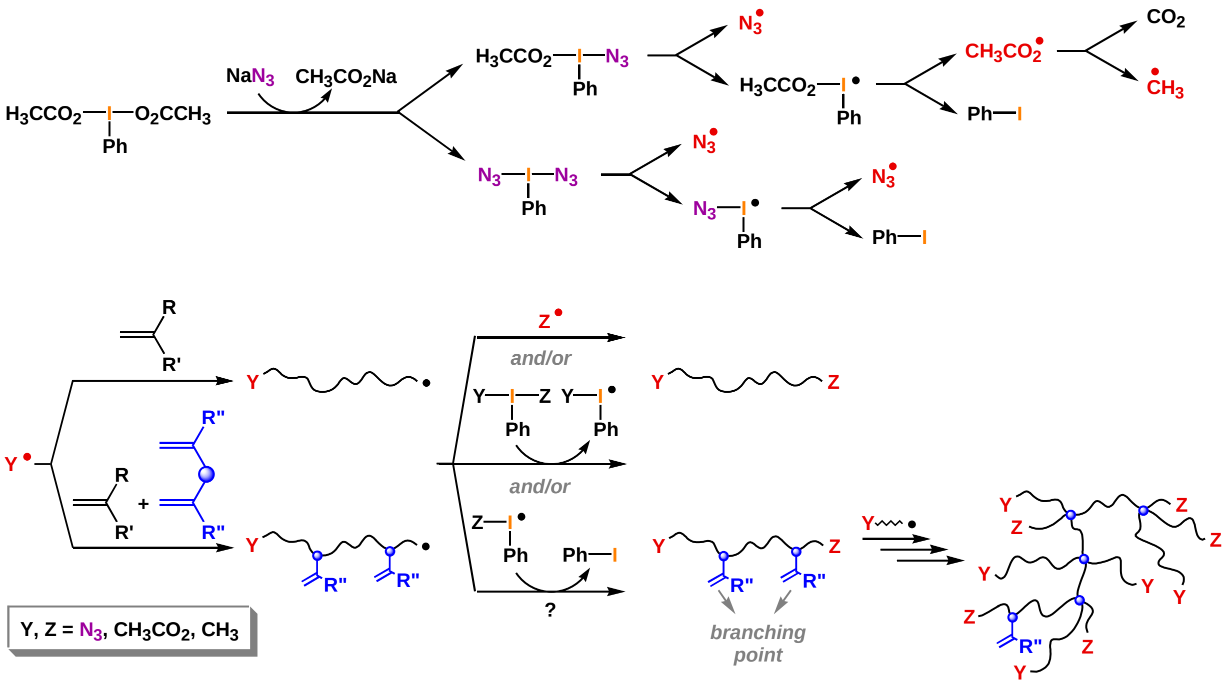


Figure 1. Kinetics (a, b) of polymerization of MMA initiated by mixtures of NaN_3 and DAIB (at $[NaN_3]_0$: $[DAIB]_0$ = 0, 2, 4, or 8) and SEC traces (c, d) of polymers obtained at similar monomer conversions (ca. 60 – 65 %). The molecular weights were determined using polystyrene

calibration. The polymerizations were carried out at 100 °C in PhCl (a, c) or DMAc (b, d). Dashed lines connecting the kinetic data points are only used to guide the eyes.

The lower molecular weights observed at higher concentrations of azide-containing hypervalent iodine(III) compounds are also consistent with the possibility of transfer of azide groups from these compounds to the propagating radicals (Scheme 1), as discussed in more detail below. The described initiating system yields a mixture of mono- and diazide-capped linear polymers, the later being the result of termination and/or azide transfer reactions.



Scheme 1. Proposed mechanism for the formation of azide-capped linear and highly branched polymers by (co)polymerizations initiated by the DAIB – NaN$_3$ system.

The preliminary studies presented in Figure 1 suggested that the decomposition of azide-containing hypervalent iodine(III) compounds was very fast at 100 ^{o}C, and experiments were carried out to test the utility of the mixture of DAIB with NaN_3 to initiate polymerization at lower (closer to ambient) temperatures. At these conditions the decomposition rate of DAIB itself would be minimal[24,83] while the decomposition of the azide-containing initiating compounds formed *in situ* would still be sufficiently fast. As seen in Figure 2, the polymerizations using $[NaN_3]_0 : [DAIB]_0 = 8$ proceeded smoothly in PhCl at 40 ^oC and the monomer conversion reached ca. 60 % in 3 h and ca. 90 % in 6.5 h. At these conditions, the ligand exchange was slow, which allowed for the slow and continuous generation of azide radicals, as indicated by the almost linear first-order kinetic plot. The initial polymerization rate in DMAc was similar, but after about 1 h (ca. 30 % conversion) the reaction slowed down dramatically and eventually stopped. Polymerizations, in which the propagation is relatively slow but the initiator decomposes rapidly often cease prior to complete consumption of the monomer. The exact value of the limiting conversion depends on the values of the propagation, termination, and initiator dissociation rate coefficients, as well as on the efficiency of initiation at the reaction temperature.[84] The propagation rate coefficient of MMA decreases by about a factor of 4 as the polymerization temperature is decreased from 100 ^oC (k_p = 1,950 M^{-1} s^{-1}) to 40 ^oC (k_p = 490 M^{-1} s^{-1}).[85] The decomposition of the initiator ($PhI(N_3)(O_2CCH_3)$ and/or $PhI(N_3)_2$) is fast at both temperatures, but the exact temperature dependence is unknown. The lower limiting conversion observed at 40 ^oC (ca. 45 %) than at 100 ^oC (ca. 65 %) in DMAc was the result of the different effect of the reaction temperature on all mentioned reaction parameters and is not unexpected.

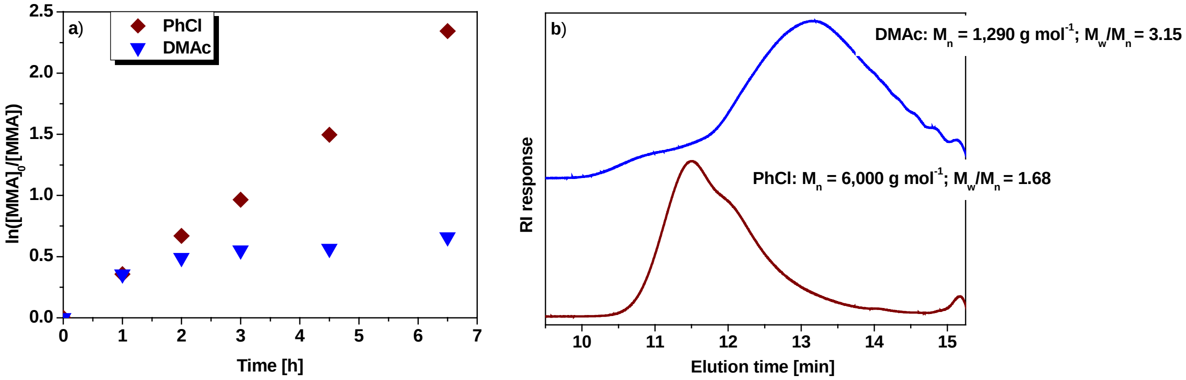


Figure 2. a) Kinetics of polymerization of MMA in presence of $[NaN_3]_0$: $[DAIB]_0$ = 8 in PhCl and DMAc at 40 °C. b) SEC traces of the polymers obtained after 1 h of polymerization (ca. 30 % monomer conversion) in each solvent. The molecular weights were determined using polystyrene calibration.

Similar to the high-temperature polymerizations, the polymer synthesized in DMAc had noticeably lower molecular weight than in PhCl. All reactions carried out in the presence of NaN_3 afforded a mixture of mono- and diazide-capped linear polymers, the presence of azide groups in which was confirmed spectroscopically, as shown below.

Synthesis of highly branched azide-capped polymers. When copolymerizations of mono- and di- (or multi-) vinyl monomers are conducted in the presence of large concentrations of rapidly decomposing radical sources, the gelation point is delayed owing to the efficient termination of the propagating radicals, which limits the polymer chain size.[43-45] The DAIB – NaN_3 initiating system is a good candidate for the one-pot synthesis of highly branched multi-azidated polymers, which can serve as precursors of various chain end-functionalized branched polymers. Copolymerizations of MMA and EGDMA were carried out at 40 °C in PhCl, i.e., at conditions where the formation of azide radicals was not exceedingly fast in order to minimize the bimolecular combination of azide radicals to N_2, which could lead to increased pressure in the reaction vessel. To prevent early gelation, it was still important to ensure that the rate of coupling of the growing radicals with azide radicals was sufficiently high. The proposed reaction mechanism responsible for the formation of azide-capped polymers (linear or branched) is presented in Scheme 1.

The "ligand" exchange reactions followed by decomposition of the *in-situ* formed hypervalent iodine(III) compound containing one azide and one acetoxy group affords azide and acetoxy (or methyl) radicals, whereas the exchange of both acetoxy groups with azide followed by decomposition yields only azide radicals, as shown on the upper part of Scheme 1. The radicals initiate the copolymerization and each incorporated EGDMA unit (pendant polymerizable group) can serve as a branching point. In order to limit the number of such branching points per propagating chain, efficient chain-killing reactions such as radical combination or transfer should occur.

Based on detailed studies of the kinetics (including kinetic isotope[86-88] and substituent effects[87,89-91]) and the distribution of reaction products[86,92,93] in the photochemical chlorination of hydrocarbons with $ArICl_2$, it is accepted that one of the steps involves transfer of a chlorine atom from the 10-I-3[94] compound, $ArICl_2$, to a carbon-centered radical derived from the hydrocarbon, accompanied with the formation of a transient 9-I-2 radical $ArI^{\bullet}Cl$. The transfer of a chlorine atom from $ArICl_2$ to cyclohexyl radicals is rather efficient and is characterized by a rate constant of 7.6×10^7, 8.0×10^7, or 8.3×10^7 M^{-1} s^{-1} for Ar = 4-$O_2NC_6H_4$, Ph, and 4-$H_3CC_6H_4$, respectively.[95] In analogy with the $ArICl_2$ compounds, $ArI(N_3)(O_2CCH_3)$ and $ArI(N_3)_2$ may also be able to transfer azide radicals to the propagating chains. Although the precise mechanism of the reaction of carbon-centered radicals with $PhI(N_3)(O_2CCH_3)$ and $PhI(N_3)_2$ will need to be elucidated further, it is plausible to assume that transfer reactions take place. The fate of the intermediate 9-I-2 radicals $PhI^{\bullet}N_3$ and $PhI^{\bullet}(O_2CCH_3)$ formed *via* homolysis of one of the hypervalent bonds in the starting 10-I-3 compound and/or azide transfer to a growing radical is even less clear. Whether and to what extend transfer reactions from these radicals to the propagating chains occur is to be ascertained by detailed mechanistic studies; the transfer is presented in Scheme 1 for completeness.

Figure 3a shows the kinetics and Figure 3b shows the evolution of molecular weight distribution (MWD) dispersities (M_w/M_n) of polymers obtained in the copolymerization of MMA with various amounts of crosslinker, EGDMA (1, 2, 5, 7.5, and 10 mol % vs. MMA), initiated by DAIB – NaN_3 (1:8) at 40 °C.

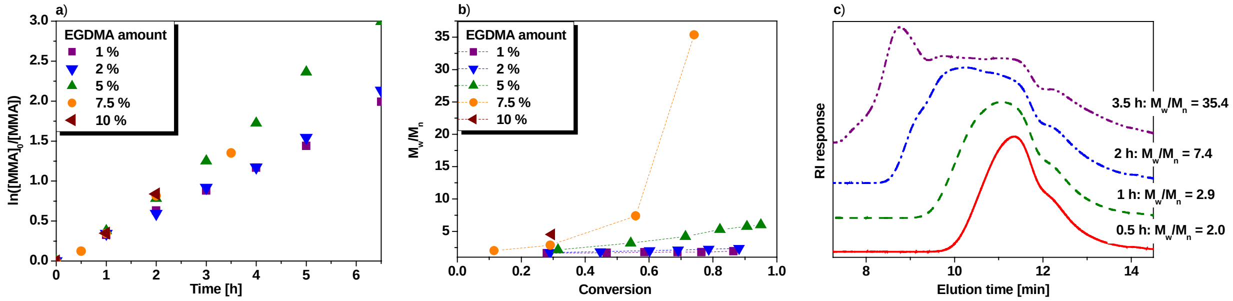


Figure 3. a) Kinetics of polymerization of MMA in the presence of 1, 2, 5, 7.5, and 10 mol % of EGDMA in PhCl at 40 °C initiated by a mixture of NaN_3 and DAIB (8:1). b) Evolution of the polymer molecular weight distribution dispersity. c) Evolution of SEC traces of b-poly$MMA(N_3)_x$ prepared using 7.5 mol % of EGDMA.

The reaction rates were not significantly affected by the amount of dimethacrylate, but the molecular weight distributions became increasingly broad as the amount of crosslinker increased. Notably, the reaction carried out with 7.5 mol % of crosslinker yielded a highly branched soluble polymer with $M_w/M_n > 35$ at 74 % conversion. Figure 3b shows the evolution of the MWDs (SEC traces) of the branched polymers obtained in the copolymerization of MMA with the largest amount of crosslinker, which could be carried out to high monomer conversion (7.5 mol % vs. MMA). The data is consistent with the increasing degree of branching during the polymerization. When the amount of EGDMA was increased to 10 mol % vs. MMA, gelation occurred at about 30 % conversion. In the absence of efficient “chain-killing” reactions, i.e., in the absence of a source of large concentration of radicals, in systems containing even as low as 1 % of crosslinker, macroscopic gelation took place at low (< 10 %) conversion.

Analysis and functionalization of the azide-capped polymers. The presence of azide groups in the prepared linear and branched polymers was proved by IR spectroscopy, elemental analysis, thermogravimetric analysis, and the ability to carry out azide-alkyne “click” chemistry reactions. After multiple steps of purification of the final polymers, films were cast on NaCl plates and IR spectra were collected, in which the absorption at 2,106 cm^{-1} corresponding to the asymmetric stretching vibration of azide groups was clearly visible (Figure 4a).

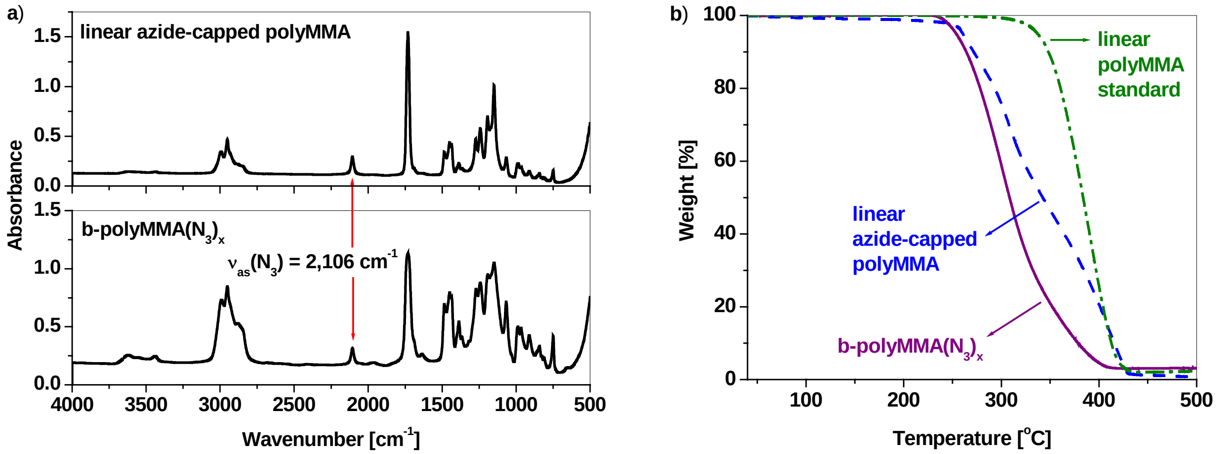


Figure 4. Characterization of azide-containing polymers: a) IR spectra of films of linear azide-capped polyMMA (top) and b-polyMMA(N_3)$_x$ obtained using 7.5 % of EGDMA vs. MMA (bottom). Both polymers were prepared in PhCl at 40 °C using [NaN_3]$_0$: [DAIB]$_0$ = 8 at 74-75 % conversion. b) TGA of azide-capped linear and branched polyMMA and a linear polyMMA standard.

The linear and branched azide-containing polymers were also analyzed by TGA (Figure 4b), which showed that the presence of thermally labile azide functionalities at the chain ends led to earlier start (lower temperature) of chain degradation compared to a linear polyMMA standard, which did not contain azide groups. The shape of the degradation curve of the linear azide-capped polymer was likely determined by the presence of azide-free chains in the sample.

Elemental analysis was used to estimate the amount of azide groups in the linear and branched polymers. The linear azide-capped polyMMA prepared in PhCl at 40 °C using [NaN_3]$_0$: [DAIB]$_0$ = 8 and isolated at 75 % conversion contained 1.98 wt % of N, corresponding to 1 azide group for about every 21 MMA repeat units. The molecular weight of the polymer was determined as 2,780 g mol^{-1} (using polyMMA-based SEC calibration) and therefore the average number of azide groups per chain was 1.3. The azide groups were situated at the chain ends, but some chains could contain 2, 1, or even 0 azide end-groups, depending on the nature of the initiating species (azide or acetoxy, or methyl radical) as well as on the chain-killing reaction (termination with azide, acetoxy, or methyl radical, transfer of azide group from $PhI(N_3)(O_2CCH_3)$ and $PhI(N_3)_2$, or bimolecular termination of two propagating chains by coupling or disproportionation). The azide-containing highly branched polymer obtained from the reaction mixture containing 7.5 mol % of EGDMA vs. MMA (3.5 h, 74 % monomer conversion) contained 0.48 wt % of N or approximately 1 azide group per 87 MMA repeat units. It should be noted that the azide groups were situated mostly at the ends of the interconnected chains, but addition of azide radicals to some of the pendant double bonds could lead to the incorporation of pendant azide groups.

As Scheme 1 suggests, the highly branched polymers are likely to contain a certain amount of unreacted pendant double bonds. They could be seen by NMR spectroscopy (Figure 5). The pendant polymerizable groups may lead to crosslinking, particularly upon prolonged storage of the polymers, and it is desirable to remove them. This could easily be accomplished by the addition of bromine to a solution of the polymer. Within several hours, bromine adds across the double bonds as proved by the disappearance of the NMR signal of the vinyl protons.

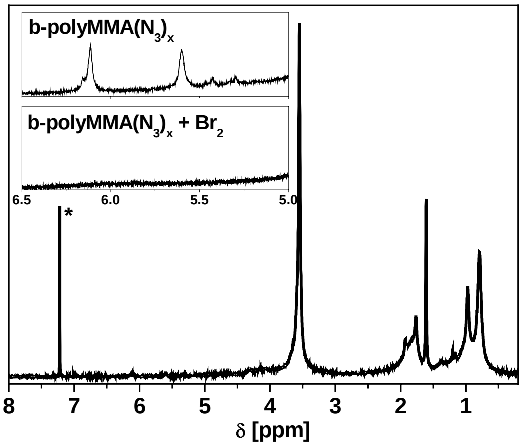
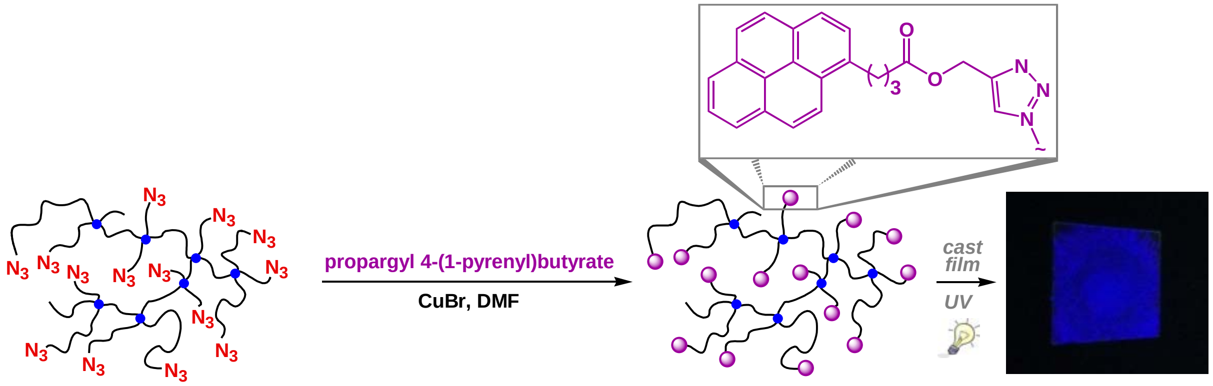


Figure 5. NMR spectrum of b-polyMMA(N_3)$_x$ obtained using 7.5 mol % of EGDMA (25 mg) in $CDCl_3$ (1 mL) before and 5 h after addition of 1 drop of Br_2. The asterisk indicates the solvent (chloroform) peak.

Another way to prove the presence of covalently attached azide groups in the hyperbranched polymers is to carry out "click"-type modification with a functional alkyne. An alkyne containing the highly fluorescent pyrenyl group, namely propargyl 4-(1-pyrenyl)butyrate was chosen for the reaction (Scheme 2).



Scheme 2. Synthesis of pyrene-labeled hyperbranched polymers by "click"-type modification of multiazidated highly branched polymers.

The copper(I)-catalyzed "click" reaction between b-polyMMA(N_3)$_x$ (prepared from a reaction mixture containing 7.5 % of EGDMA vs. MMA) and the pyrene-containing alkyne afforded bright yellow-colored polymers. The pyrene-labeled hyperbranched polymer was analyzed by NMR spectroscopy (Figure 6a), from which the ratio of the pyrene and linker triazole groups (with proton resonances at 8.3 – 7.6 ppm) to MMA repeat units was determined to be 1 : 94. This ratio is very close to the ratio of azide groups to MMA repeat units of 1 : 87, determined by elemental analysis of the starting material, indicating the very high efficiency of the "click"-type attachment of pyrene groups to the polymer chain ends.

The pyrene-containing polymer was highly fluorescent, similar to the low-molecular-weight pyrene derivative. Somewhat brittle films could be cast from $CHCl_3$ solution of the polymer, which showed blue fluorescence upon irradiation with UV light, as shown in Scheme 2. The emission spectra (normalized with respect to the most intense peak) of solutions of the polymer in various solvents are presented in Figure 6b. The concentration of the solutions was 0.1 mg mL^{-1}, which, based on the NMR analysis, corresponded to 3.33 μg mL^{-1} of groups derived from the acetylene-containing pyrene (propargyl 4-(1-pyrenyl)butyrate). Due to the presence of a number of closely situated pyrene residues in the polymer, an emission band around 480 nm was observed, which was likely the result of formation of excimers.[96] The emission at 480 nm was more intense relative to the main emission at 400 nm in the weakly polar THF and $CDCl_3$, and less intense in the more polar DMF and DMSO. The emission characteristics of the low-molecular-weight pyrene-containing compound in THF were also studied, for comparison with the polymer, at a concentration corresponding to that of the pyrene groups in the polymer solution (3.33 μg mL^{-1}). The spectrum did not show excimer formation.

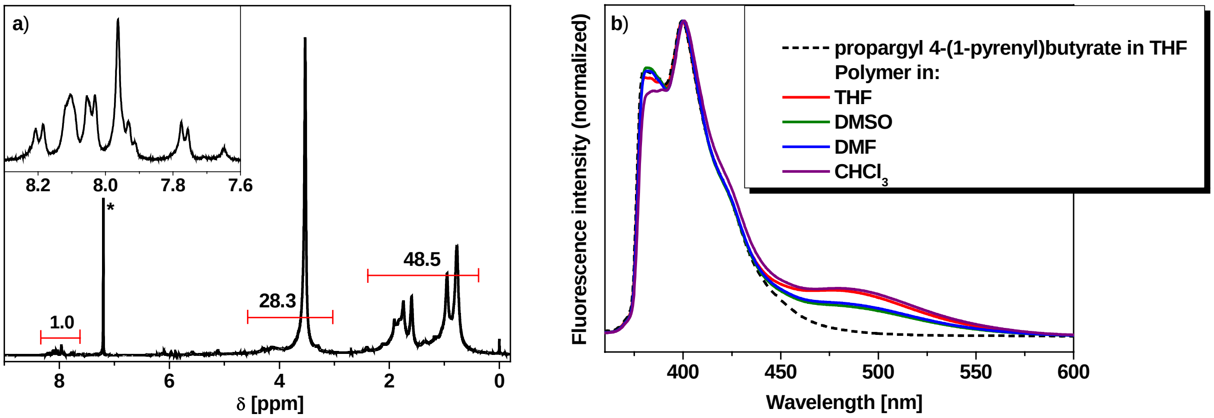


Figure 6. a) NMR spectrum (128 scans) of pyrene-modified hyperbranched polyMMA (prepared using 7.5 % cross-linker vs. MMA) in $CDCl_3$ (2 mg mL^{-1}). The asterisk indicates the solvent (chloroform) peak. b) Fluorescence spectra of propargyl 4-(1-pyrenyl)butyrate in THF (3.33 µg mL^{-1}) and the pyrene-labeled polymer (0.1 mg mL^{-1}) in various solvents.

Pyrene containing materials are appealing due to their potential applications as optical switches,[97-99] in optical recording,[100,101] piezochromic materials,[102] solar cells,[103,104] and various sensors for small molecules or ions.[105] As shown, the DAIB – NaN_3 system provides an easy access to pyrene-labeled materials. Due to the reactivity of the azide group, many other functional polymers with either linear or branched molecular architecture can be synthesized as well.

Conclusions

A novel one-pot method was developed for the synthesis of mono- and diazide-capped linear and multiazidated hyperbranched polymers that utilizes the “ligand” exchange reaction between (diacetoxyiodo)benzene and sodium azide, followed by decomposition of the newly formed hypervalent iodine(III) compounds with azide ligand(s). The azide radicals are generated rapidly even at moderate temperatures, and can initiate the polymerization of vinyl monomers such as methyl methacrylate, yielding azide-capped linear polymers. They also participate in termination reactions with the propagating radicals, which contributes to increased degree of chain-end functionalization. Azide-transfer from the azide-containing hypervalent iodine(III) compounds formed *in situ* to the propagating radicals plausibly also took place. When copolymerization of crosslinkers with monovinyl monomers was conducted in the presence of the DAIB – NaN_3 system, highly branched polymers were formed up to high monomer conversions, even at high concentration of the crosslinker, owing to efficient "chain-killing" reactions (termination and potentially azide transfer from the hypervalent iodine species), which limit the average number of incorporated pendant vinyl groups per chain and thus delay macroscopic gelation. The presence of azide groups in the produced polymers was proved by IR spectroscopy, elemental analysis, thermo-gravimetric analysis and the ability to carry out "click"-type chemical modifications with a fluorescent pyrene-based alkyne.

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