



Polymer
Chemistry

**Hypervalent Iodine-Based Dynamic and Self-Healing
Network Polymers**

Journal:	<i>Polymer Chemistry</i>
Manuscript ID	PY-ART-05-2019-000664.R1
Article Type:	Paper
Date Submitted by the Author:	24-Jun-2019
Complete List of Authors:	Vaish, Avichal; Southern Methodist University, Chemistry Tsarevsky, Nicolay; Southern Methodist University, Chemistry

SCHOLARONE™
Manuscripts

ARTICLE

Hypervalent Iodine-Based Dynamic and Self-Healing Network Polymers

Avichal Vaish and Nicolay V. Tsarevsky*

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Linear polymers with multiple carboxylate pendant groups (copolymers of styrene and acrylic acid) participate in ligand-exchange reactions with (diacetoxyiodo)benzene and the reaction yields network polymers with (diacyloxy)iodoarene-type crosslinks. The unreacted carboxylate groups that are present in the polymers can participate in further ligand-exchange reactions with the hypervalent iodine(III) centers at the crosslinks, which makes the materials dynamic and self-healing. The application of strong shear force leads to gel disintegration but when the external force is removed, the gels are regenerated again, as proved by rheology studies. When exposed to UV light or heat (microwave irradiation), the gels are “set” (i.e., become permanent) due to the homolytic cleavage of the weak hypervalent I-O bonds present at the crosslinks, followed by irreversible radical coupling of adjacent polymer-bound C- and/or O-centered radicals.

Introduction

The design and preparation of dynamic polymers formed as a result of reversible covalent interactions is of great interest¹⁻¹⁶ since these materials often possess unique properties, which makes them attractive for various applications, such as controlled drug delivery systems,¹⁷ adaptive surfaces,⁵ polymeric actuators,¹⁸ and self-healing materials.¹⁹⁻²⁸ Self-healing is the process, in which a material that had been damaged by mechanical forces can acquire its original properties (and often appearance) without external treatment, such as the application of additional reagents. The process occurs due to the presence of reactive functionalities, which are responsible for the formation of new bonds, typically but not necessarily identical to the ones that had been cleaved during the damage.²⁹⁻³⁹ If the self-healing is efficient and faster than the propagation of further defects, it improves the reliability of the material, extends its life-time, makes costly repairs unwarranted, and often reduces safety risks by preventing failures caused by the accumulation of cracks or breaks. Electrostatic (ionic) interactions,^{40, 41} hydrogen bonds,^{42, 43} as well as coordination bonds^{44, 45} have all been utilized in the design and preparation of dynamic and self-healing polymers.

Many main-group elements form compounds, in which the octet rule is not obeyed, and in which the central polyvalent atom is bonded to some of the “ligands” via 3-center-4-electron, dubbed hypervalent (HV),⁴⁶ bonds. These bonds are weaker than the “classical” covalent (2-center-2-electron) bonds and are typically rather polar.⁴⁶⁻⁴⁸ As expected based on the number of unpaired electrons in the ground state, iodine is often monovalent in its compounds. However, numerous

examples are known, in which the iodine atom is polyvalent, e.g., tri-, penta-, or heptavalent, and participates in the formation of one covalent and several additional HV bonds. HV iodine compounds are primarily used as oxidizing agents⁴⁹⁻⁵² and in other electrophilic and radical reactions, including as initiators for cationic⁵³⁻⁵⁵ and/or radical⁵⁶⁻⁵⁹ polymerizations. The HV bonds in the fragment L-I-L in the iodine(III) compound of the type ArIL₂ (Ar is aryl, and the ligand L is (pseudo)halide, carboxylate,⁶⁰ or tetrazolate⁶¹) are dynamic in nature⁶² and the ligands, L can be easily (and typically reversibly) displaced by nucleophiles Nu⁻. The reaction affords, depending on the amount of added nucleophile and the reaction time, ArI(L)Nu and/or ArINu₂ as well as free L⁻.⁶³ For example, (diacyloxyiodo)arenes ArI(O₂CR¹)₂ (Ar = aryl, R = alkyl or aryl) participate in ligand-exchange reactions with carboxylates R²CO₂⁻ or the corresponding acids R²CO₂H to yield first the asymmetric compound ArI(O₂CR¹)(O₂CR²) and eventually ArI(O₂CR²)₂, as well as free R¹CO₂⁻ or R¹CO₂H. The thermodynamics and kinetics of this type of reaction involving (diacetoxyiodo)benzene PhI(O₂CCH₃)₂ were studied spectroscopically (with R²CO₂H being methacrylic⁶⁴ or acrylic acid⁶⁵) and it was shown that the ligand exchange is relatively fast even in dilute solutions. The reaction of PhI(O₂CCH₃)₂ with methacrylic acid was employed to synthesize branched polymers via the generation (*in situ*) of inimers with methacryloyloxy groups attached to the HV iodine(III) center. More recently, stimuli-responsive and reductively degradable branched polymers were reported containing (diacyloxyiodo)arene groups as structural elements, i.e., at each branching point connecting two linear chains.⁶⁵ The addition of acetic acid to solutions of these polymers led to fast degradation and it was speculated that the degradation induced by ligand-exchange with free carboxylates could be reversible, i.e., that the materials could be dynamic in nature.

Department of Chemistry, Southern Methodist University, 3215 Daniel Avenue, Dallas, TX 75275, USA. E-mail: nvt@smu.edu

*Electronic Supplementary Information (ESI) available: polymerization kinetics, characterization data, and video of self-healing. See DOI: 10.1039/x0xx00000x

Herein, we report the preparation of dynamic gels by substitution of the acetoxy groups in $\text{PhI}(\text{O}_2\text{CCH}_3)_2$ by polymer-bound carboxylate groups. The presence of multiple unreacted pendant carboxylate groups, which can participate in ligand-exchange reactions with the HV iodine(III) centers at the crosslinking points, makes the materials both dynamic and self-healing. Further, advantage is taken of the fact that HV iodine(III) compounds ArIL_2 decompose homolytically upon irradiation or heating with the formation of the monovalent iodine compound, iodoarene ArI , and the radicals L^\bullet ,^{50, 55, 58, 59, 66-68} which can react with a substrate or couple. The coupling reaction between the macromolecular carboxylate radicals and/or the alkyl radicals that are formed by their decarboxylation can reasonably be expected to yield irreversibly the formation of permanently crosslinked polymers. The feasibility of this approach, which converts the dynamic to "set" gels, and which provides flexibility to use the same polymer network for various applications, is demonstrated.

Experimental Section

Materials

Styrene (Sty, 99%, Alfa Aesar) and *tert*-butyl acrylate (tBA, 98%, Aldrich) were purified before the polymerizations by passing through a column filled with basic alumina to remove the inhibitor. The radical initiator, 1,1'-azobis(cyclohexanecarbonitrile) (ACHN, 98%, Aldrich), anisole (99%, Acros), $\text{CF}_3\text{CO}_2\text{H}$ (99%, Aldrich), $\text{PhI}(\text{O}_2\text{CCH}_3)_2$ (98%, Acros), glacial $\text{CH}_3\text{CO}_2\text{H}$ (99.7%, Fisher), NaN_3 (99.5%, Aldrich), tri-*n*-butylphosphine (Bu_3P , 95%, Alfa Aesar), indigo carmine (> 80%, Fisher), *N,N*-dimethylacetamide (DMAc, 99%, Alfa Aesar), 1,4-dioxane (99.8%, Alfa Aesar), dichloromethane (99%, Fisher), methanol (MeOH, 99%, Fisher), and tetrahydrofuran (THF, 99.5%, EMD Millipore) were used as received. The chain transfer agent, (2-(((butylthio)carbonothioyl)thio)-2-methylpropanoic acid (BMP), was synthesized by following a reported method.⁶⁹ Cobalt Blue was prepared by first drying a mixture of cobalt(II) and aluminum hydroxides (1:2 molar ratio) at 120 °C for 40 h and then calcining the obtained material at 1000 °C for 6 h.⁷⁰ The deuterated solvents, acetone- d_6 (99.9% D, Cambridge Isotope Laboratories) and DMSO- d_6 (99.9% D, Cambridge Isotope Laboratories), contained a small amount of tetramethylsilane (TMS) as the chemical shift reference.

Analyses and characterization methods

Molecular weights and molecular weight distribution (MWD) dispersities ($\text{Đ} = M_w/M_n$) 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. The total monomer conversion was determined by ^1H NMR spectroscopy, using a

Bruker Avance DRX (400 MHz) or a JEOL ECCA (500 MHz) spectrometer, by monitoring the decrease of the sums of intensities of the vinyl peaks (from Sty and tBA) relative to the intensity of the methoxy protons of anisole (internal standard present in the reaction mixtures). Rheological data was obtained by using a Discovery Hybrid HR-3 rheometer (TA instruments) with cone plate geometry (diameter of 40 mm, cone angle 2° 00' 32", truncation gap 53 μm). All rheological measurements were carried out at 25 °C, which was controlled with a Peltier thermo-module unit. The entire plate was covered with sample (2 mL) for consistent results and the measurements were performed 30 min after mixing of the components of the gel. Photochemical curing was conducted by either UVP CL-1000L UV crosslinker (365 nm) or Ushio G20T10 low pressure mercury arc UV lamps (254 nm, 21 W). Thermal curing was carried out in a CEM Discover SP microwave reactor (300 W). The time-lapse video of gel healing was taken by using AmScope optical microscope and MD600E camera.

Synthetic procedures

Synthesis and characterization of poly(Sty-*co*-tBA). Random copolymer of Sty and tBA with equal monomer feed ratio was synthesized by mixing Sty (15 mL, 0.131 mol), tBA (19.16 mL, 0.131 mol), BMP (0.0264 g, 1.05×10^{-4} mol), ACHN (0.0128 g, 5.24×10^{-5} mol), and anisole (internal standard, 2 mL) in a round bottom flask equipped with magnetic stir bar. The flask was sealed with a rubber septum and was placed in an ice-water cooling bath in order to minimize evaporation of the reaction components during the following purging with nitrogen. The reaction mixture was deoxygenated by purging with nitrogen for 20 min. The flask was then immersed in an oil bath at 85 °C and samples were withdrawn from the mixture at timed intervals with a nitrogen-purged syringe for ^1H NMR analysis (after dilution with acetone- d_6) or for SEC analysis (after dilution with THF). After reaching the targeted molecular weight, the polymerization was quenched by exposing the reaction mixture to air. The mixture was then diluted with CH_2Cl_2 and the polymer was precipitated in methanol. The reprecipitation was repeated two additional times, and the polymer was dried. In other experiments, the molar ratios of Sty and tBA were changed to 1:3 and 3:1, keeping the same total monomer to chain transfer agent (BMP) ratio. Polymerization kinetics as well as the evolution of molecular weights and MWD dispersities with conversion, and individual SEC traces are shown in Fig. S1 in the Supporting Information (SI).

Conversion of poly(Sty-*co*-tBA) to poly(Sty-*co*-AA) (AA = acrylic acid). Sty-tBA copolymer (0.06 mol with respect to *tert*-butyl groups, i.e., 15–20 g depending on copolymer composition) was dissolved in CH_2Cl_2 (50 mL) and $\text{CF}_3\text{CO}_2\text{H}$ (15 mL, 0.2 mol) was added to convert the *tert*-butyl ester into carboxylic acid groups. The reactions were monitored by ^1H NMR spectroscopy and after 4 h, when the methyl proton peak from the *tert*-butyl

groups (at ca. 1.5 ppm) was no longer discernable (Fig. S2), the mixture was diluted with acetone (25 mL) and the polymer was precipitated in methanol-water (2:1 (v/v)). The reprecipitation procedure was repeated once again. The polymers were then dried under vacuum for a day.

Preparation of gels with (diacyloxyiodo)benzene-type crosslinking groups. To study the formation of gels, first, a stock solution of $\text{PhI}(\text{O}_2\text{CCH}_3)_2$ (0.15 M) was prepared by dissolving the HV iodine compound (0.483 g, 1.5 mmol) in DMAc (10 mL). The second stock solution contained the carboxylate-containing copolymer in DMAc (10 mL). Due to the different solubilities of the three investigated polymers, their amounts in the stock solutions differed. The stock solution of $\text{Sty}_1\text{AA}_{0.5}$ contained 1.7 g of the polymer (corresponding to 0.58 M concentration of carboxylate groups), that of $\text{Sty}_1\text{AA}_{0.7}$ contained 1.6 g of the polymer (0.70 M of carboxylate groups), and that of $\text{Sty}_1\text{AA}_{0.9}$ was prepared from 1.4 g of the polymer (0.73 M of carboxylate groups). The stock solutions of the two gel precursors, in some cases, after dilution with DMAc, were mixed at different ratios. It was ascertained that in all cases, the copolymer with the lowest fraction of carboxylate pendant groups, $\text{Sty}_1\text{AA}_{0.5}$, formed very loose gels, which could not be taken out of the reaction vials and could not be subjected to rheological measurements. The gels prepared from the copolymer with the highest fraction of carboxylate groups, $\text{Sty}_1\text{AA}_{0.9}$, formed quickly but were not uniform or “homogenous”, and were not suitable for rheological studies that yielded consistent and reproducible results. However, the dynamic properties of a gel prepared by mixing the mentioned $\text{Sty}_1\text{AA}_{0.9}$ stock solution and the $\text{PhI}(\text{O}_2\text{CCH}_3)_2$ stock solution (3:2 (v/v)) could be examined visually (Fig. 1). The gels derived from $\text{Sty}_1\text{AA}_{0.7}$ (intermediate fraction of carboxylate groups) were the most homogeneous. Gels that could be studied both visually (Fig. 2) and by rheology (Fig. 3) were prepared by mixing that copolymer solution (0.35 M of carboxylate groups, prepared after dilution of the stock solution with DMAc) with $\text{PhI}(\text{O}_2\text{CCH}_3)_2$ stock solution (4:1 (v/v)).

The stability of some of the prepared gels with respect to monocarboxylic acids ($\text{CH}_3\text{CO}_2\text{H}$), azides, and phosphines was examined by adding various amounts of the mentioned reagents to the swollen gels, as described in the Results and Discussion section.

In some cases, to achieve better visibility of the gels, a small amount of indigo carmine was added, but, due to the tendency of this dye to change color and fade over time in the presence of the components of the gels, most of the colored gels were prepared using Co Blue (selected because of its stability in the presence of many reagents, including oxidants⁷⁰).

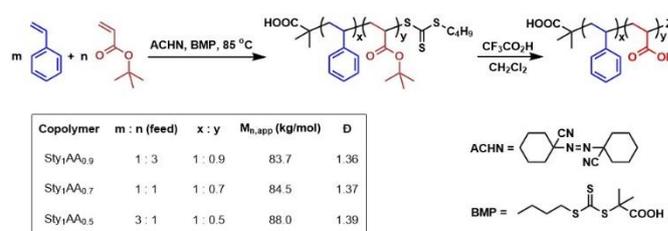
Conversion of dynamic to non-dynamic (permanent, “set”) networks by irradiation with UV light. The gels were prepared by mixing 300 μL of $\text{Sty}_1\text{AA}_{0.9}$ solution (0.73 M with respect to carboxylate groups) with 200 μL of $\text{PhI}(\text{O}_2\text{CCH}_3)_2$ solution (0.15

M) in DMAc in a glass tube. After 10 min, the glass tube was exposed to UV light (UVP CL-1000L UV crosslinker, 365 nm) for 30 min. Subsequently, 500 μL of DMAc was added to the tube along with 100 μL of glacial $\text{CH}_3\text{CO}_2\text{H}$ to check the stability of the network.

Larger amounts of gels were prepared by mixing 400 μL of $\text{PhI}(\text{O}_2\text{CCH}_3)_2$ (0.15 M) solution with 1600 μL of $\text{Sty}_1\text{AA}_{0.7}$ (0.35 M) solution in DMAc in a 10 mL glass beaker. After 10 min of mixing, the gel was cured by exposing it to two low pressure mercury arc UV lamps (254 nm, 21 W) for 90 min. The light source was kept ca. 5 inches above the surface of the gel. After curing, the gel was washed twice with 1 mL of DMAc to remove the byproducts (e.g., iodobenzene and the products of its photochemical decomposition) and the gel was subjected to rheological examination.

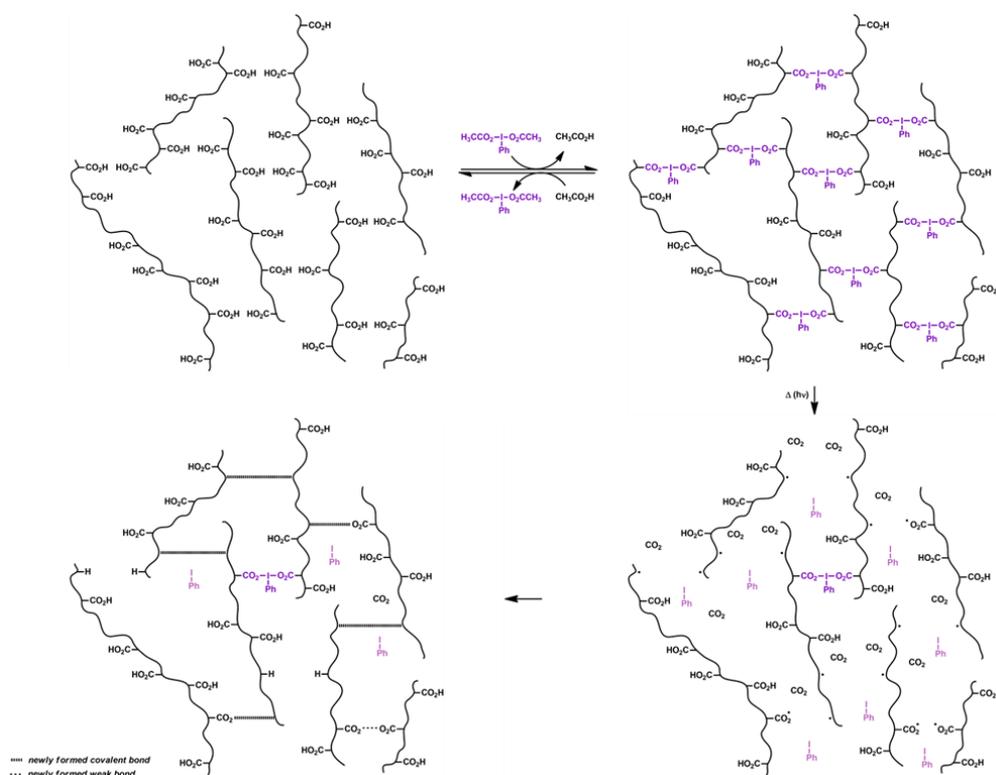
Conversion of dynamic to non-dynamic (permanent, “set”) networks by thermal curing. Gels were prepared by mixing 300 μL of $\text{Sty}_1\text{AA}_{0.9}$ solution (0.21 M with respect to carboxylate groups) with 200 μL of freshly-prepared $\text{PhI}(\text{O}_2\text{CCH}_3)_2$ solution (0.10 M) in 1,4-dioxane in a microwave tube, which was then kept in a microwave reactor at 200 °C for 2 min. The power was set to 300 W and the timer was started when the temperature reached 200 °C. The total reaction time (including heating and cooling) was 40 min. At the end of the procedure, the gel was washed two times with 500 μL of 1,4-dioxane, which was discarded and then 100 μL of $\text{CH}_3\text{CO}_2\text{H}$ along with 500 μL of 1,4-dioxane were added to the tube. The stability of the gel in the presence of $\text{CH}_3\text{CO}_2\text{H}$ was inspected visually just after the addition of the acid and 72 h later.

Results and Discussion



Scheme 1 Synthesis of carboxylate group-containing copolymers by copolymerization of Sty and tBA under RAFT polymerization conditions, followed by deprotection of the *tert*-butyl ester groups in the presence of $\text{CF}_3\text{CO}_2\text{H}$.

The reversible addition–fragmentation chain transfer (RAFT) polymerization^{71–74} of Sty and tBA (Scheme 1) was performed to prepare three different random copolymers – $\text{Sty}_1\text{tBA}_{0.9}$, $\text{Sty}_1\text{tBA}_{0.7}$, and $\text{Sty}_1\text{tBA}_{0.5}$, where the numbers indicate the molar ratios of the monomer units in the final isolated copolymers (determined by ¹H NMR spectroscopy). The polymerizations were carried out in bulk at 85 °C for 40–50 h, depending on the monomer feed ratio. ACHN was chosen as initiator because of its relatively long half-life time at the conditions of the experiment (the reported value is 16 h at 85 °C in toluene⁷⁵). BMP was used as the chain transfer agent, which controls



Scheme 2 Preparation of dynamic gels via carboxylate ligand-exchange reactions with $\text{PhI}(\text{O}_2\text{CCH}_3)_2$, curing of the gels using light or heat, and conversion of the dynamic to permanent network following the coupling of some of the radicals formed during the curing step.

well the polymerization of both acrylates and styrenes. As the polymerizations proceeded, the number-average molecular weights ($M_{n,\text{app}}$) increased and the MWDs narrowed (Fig. S1). After purification of the random copolymers, the *tert*-butyl ester groups were removed using $\text{CF}_3\text{CO}_2\text{H}$. The apparent molecular weights of all three copolymers after the deprotection were similar (83,700–88,000 g/mol).

Preparation of dynamic gels

(Diacyloxyiodo)arenes can participate in ligand-exchange reactions with various nucleophiles, including carboxylates. This reaction was taken advantage of and dynamic networks were prepared by displacing the acetoxy ligands in $\text{PhI}(\text{O}_2\text{CCH}_3)_2$ by

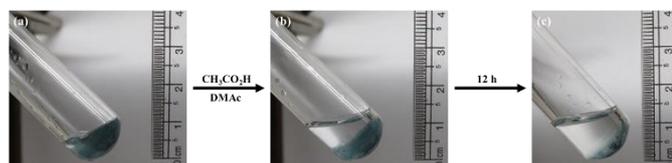


Fig. 1 Dynamic gel 15 min after mixing copolymer $\text{Sty}_1\text{AA}_{0.9}$ (300 μL , 0.73 M with respect to carboxylate groups) and $\text{PhI}(\text{O}_2\text{CCH}_3)_2$ (200 μL , 0.15 M) solutions (a); gel immediately after addition of DMAC and $\text{CH}_3\text{CO}_2\text{H}$ (600 μL , 5:1 (v/v)) (b); and degraded gel 12 h after the addition of $\text{CH}_3\text{CO}_2\text{H}$ (c). The precipitate on the bottom of the tube consists of Co Blue.

the pendant carboxylate groups in poly(*Sty-co-AA*), as shown in Scheme 2. Three different poly(*Sty-co-AA*) copolymers (designated $\text{Sty}_1\text{AA}_{0.9}$, $\text{Sty}_1\text{AA}_{0.7}$, and $\text{Sty}_1\text{AA}_{0.5}$, as explained in

Scheme 1) were prepared by removal of the *tert*-butyl ester groups in the poly(*Sty-co-tBA*) precursors by treatment with $\text{CF}_3\text{CO}_2\text{H}$. A dynamic gel was then prepared by mixing 200 μL of $\text{PhI}(\text{O}_2\text{CCH}_3)_2$ (0.15 M) and 300 μL of $\text{Sty}_1\text{AA}_{0.9}$ (0.73 M with respect to carboxylate groups) solutions in DMAC, with or without addition of trace amounts of indigo carmine or Co Blue (used for better visualization). Once the gel was formed, the HV iodine center could exchange ligands with unreacted carboxylate acid groups, or external nucleophiles. The formation of network polymers and their transformations in the presence of monocarboxylic acids, or upon irradiation or heating are presented in Scheme 2. The $\text{Sty}_1\text{AA}_{0.5}$ copolymer did not form a gel with $\text{PhI}(\text{O}_2\text{CCH}_3)_2$, most likely due to insufficient amount of accessible carboxylate pendant groups in the copolymer.

To confirm the dynamic nature of the network polymers, $\text{CH}_3\text{CO}_2\text{H}$ (100 μL , 1.75 mmol, 58 eq. vs. the originally employed $\text{PhI}(\text{O}_2\text{CCH}_3)_2$) was added after washing the gel twice with DMAC and, as expected, the gel completely disintegrated in 12 h to yield the initial copolymer and $\text{PhI}(\text{O}_2\text{CCH}_3)_2$, as shown explained in Scheme 1 (top) and as shown in Fig. 1.

The same experiment was repeated with azide as a nucleophile and the gel degraded, as shown in Fig. S3a–b (SI). This reaction yields the very unstable $\text{PhI}(\text{N}_3)_2$,⁷⁶ which decomposes readily with the formation of iodobenzene PhI and the highly reactive azide radicals.⁷⁷ The dynamic gel also disintegrated after addition of reducing agents, such as Bu_3P , which reduces iodine(III) to iodine(I),⁷⁸ i.e., PhI (Fig. S3c–d). This reductive degradation in the presence of Bu_3P was recently

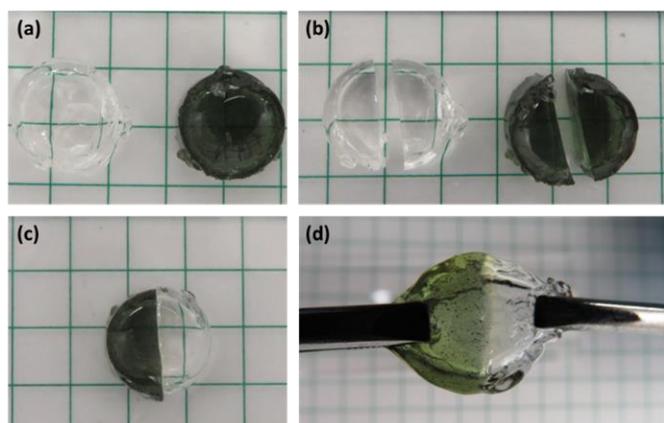


Fig. 2 Gels prepared by mixing solutions of Sty₁AA_{0.7} (400 μ L, 0.35 M with respect to carboxylate groups) and PhI(O₂CCH₃)₂ (100 μ L, 0.15 M) in DMAc with trace amount of indigo carmine present in one of the gels (a); the gels cut into two pieces (b); reattached semicircular segments taken from the two pieces of gels after 30 min (c); and effect of stretching on the self-healed gel (d).

demonstrated to occur in closely-related branched polymers with (diacyloxyiodo)benzene groups at the branching points.⁶⁵

Self-Healing and Rheological Properties of Dynamic Gels

After establishing the dynamic nature of the gels, their ability to self-heal was examined. In a preliminary experiment, two disk-shaped gels were prepared by mixing 400 μ L of Sty₁AA_{0.7} (0.35 M) solution and 100 μ L of PhI(O₂CCH₃)₂ (0.15 M) solution in DMAc, one of which contained a minuscule amount of indigo carmine dye to provide color difference, in a cylindrical container. Gelation occurred within ca. 10 min and the gels were transparent in appearance (Fig. 2). Then, the disk-shaped

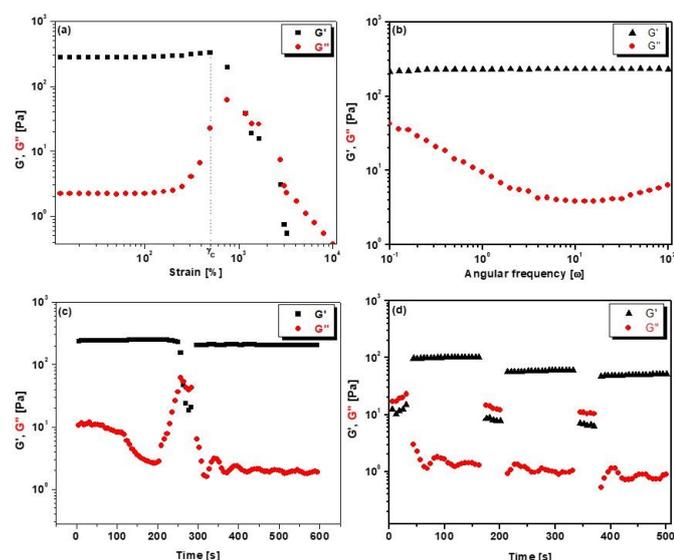


Fig. 3 G' and G'' values of a gel prepared by using Sty₁AA_{0.7} and PhI(O₂CCH₃)₂ in DMAc (a) on strain amplitude sweep; (b) on angular frequency sweep; (c) in time-dependent strain sweep measurement, in which, strain was gradually increased from 0.1% to 1300% and then back to 1% strain for 300 s; (d) in continuous step strain measurement, gel was subjected to 1300% strain for 30 s, then go back to 1% strain in the linear regime for 120 s, and 3 cycles were carried out.

gels were cut in halves and the pieces were swapped and kept in contact for 30 min without any external pressure. The free carboxylate groups and HV crosslinks present on the surface of one piece of cut gel could participate in ligand-exchange with HV iodine centers on the other piece, which led to re-formation of the network. The cut between the two original semi-cylindrical pieces became invisible after 30 min and the healed gel did not break at the conjoining line even upon stretching. The self-healing was also monitored under an optical microscope and a time-lapse video showing healing of the cut was recorded and can be found in the SI.

The self-healing was then quantified by rheological measurements (Fig. 3). The elastic response of the crosslinked network was analyzed first by strain amplitude sweep to determine the linear viscoelastic regime of the gel. In this experiment (Fig. 3a), the storage and loss moduli (G' and G'' , respectively) were recorded as a function of the strain (γ) at a constant angular frequency ($\omega = 10$ rad/s). It was noticed that, in the viscoelastic region, *i.e.* 0.1% to ca. 500% strain, G' was constant and greater than G'' but, above a critical strain ($\gamma_c \approx 500\%$), it rapidly began to decline, which suggested the collapse of the crosslinked network. When the strain was increased to over 1200%, the values of G' became lower than G'' , which suggested that virtually no crosslinking between the polymer chains had been retained. At this point, the gel behaved like a viscoelastic liquid rather than a solid. In another experiment, the rheological behavior of the gel was assessed by subjecting it to increasing angular frequency ($\omega = 0.1$ -100 rad/s) at a constant strain (1%), which was in the viscoelastic regime. The G' values (ca. 230 Pa) were independent of ω and larger than the G'' values over the entire range of angular frequencies (Fig. 3b), which affirmed the re-formation of gel.^{79, 80}

After the preliminary rheological experiments, self-healing was confirmed by time-dependent strain sweep and continuous step-strain measurements. In the time-dependent strain sweep experiment (Fig. 3c), at first the strain was increased gradually, from 0.1 to 1300%, to break the network and then the strain was reduced to 1% for 300 s at a constant angular frequency ($\omega = 10$ rad/s). Interestingly, the gel exhibited a swift recovery of the mechanical strength after large amplitude oscillatory breakdown. The gel recovered ca. 85% of its original G' values in less than 20 s, which demonstrated efficient and rapid self-healing. Furthermore, continuous step-strain measurements were conducted to quantify the reproducibility of the self-healing. In this experiment, the gel was subjected to 1300% strain for 30 s and then the strain was decreased to 1% for 120 s. This cycle was repeated three times. When nonlinear, large amplitude oscillations ($\gamma = 1300\%$ at $\omega = 10$ rad/s) were applied to the gel, the values of G' decreased to ca. 10 Pa, resulting in viscoelastic fluid-like behavior ($\tan \delta$ (G''/G') ≈ 1.5). However, when the strain was decreased to 1%, the values of G' recovered promptly (within 20 s) to ca. 100 Pa and G' values became greater than G'' values, showing quasi-solid-like behavior (Fig. 3d). Although the G' values were not completely restored after each cycle, the recovery of the gel was reproducible for at least three cycles. This was the conclusive evidence of self-healing nature of the gel.

Conversion of Dynamic to Permanent Gels

The HV I-O bonds in $\text{ArI}(\text{O}_2\text{CR})_2$ can dissociate homolytically upon irradiation or heating to yield acyloxy radicals (RCO_2^\bullet) or the products of their decarboxylation (R^\bullet), along with iodoarene ArI. This property of the HV bonds enabled the conversion of the dynamic to permanently crosslinked gel by exposing the former to UV light or heat. During this treatment, macromolecular acyloxy and eventually alkyl radicals are generated (bottom of Scheme 2). Several types of bonds can be formed by combination of the radicals: weak O-O bonds (coupling of acyloxy radicals), which can be cleaved

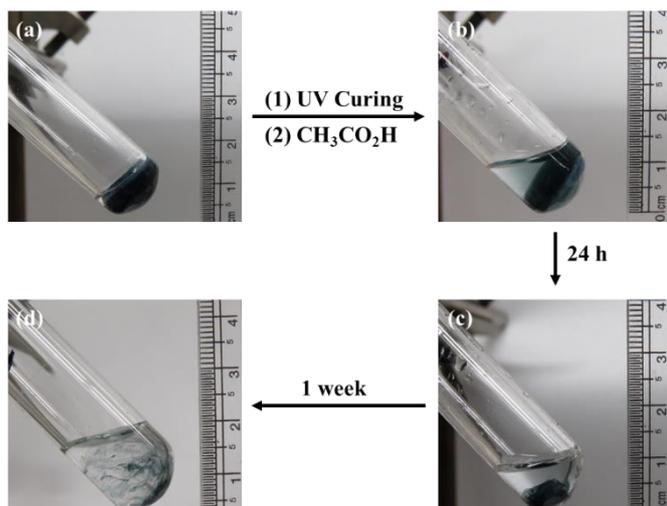


Fig. 4 a) Gel 15 mins after mixing of $\text{Sty}_1\text{AA}_{0.9}$ (300 μL , 0.73 M with respect to carboxylate groups) and $\text{PhI}(\text{O}_2\text{CCH}_3)_2$ (200 μL , 0.15 M) solutions in DMAC. b) Gel after 30 min of UV curing and addition of $\text{CH}_3\text{CO}_2\text{H}$ in DMAC (600 μL , 1:5 (v/v)). c) Washed gel 24 h after the addition of $\text{CH}_3\text{CO}_2\text{H}$ and DMAC, and d) the same swollen gel after 1 week.

homolytically again to acyloxy radicals, or the stable C-C or C-O bonds, which are actually responsible for the formation of permanent networks. The efficiencies of all these combination reactions depend on the flexibility of the polymer chains in the medium and the ease of diffusion of the macromolecular radicals. If these radicals cannot diffuse fast enough to couple, transfer reactions with the solvent are likely to occur, which would minimize and might even completely prevent the formation of permanent crosslinks.

To show the conversion of dynamic to set, non-dynamic, network, an experiment was carried out by exposing the dynamic gel, prepared by mixing 200 μL of $\text{PhI}(\text{O}_2\text{CCH}_3)_2$ (0.15 M) solution and 300 μL of $\text{Sty}_1\text{AA}_{0.9}$ (0.73 M with respect to carboxylate groups) solution in DMAC along with trace amount of Co Blue, to UV light (365 nm) for 30 min in a glass tube (Fig. 4). After curing, 500 μL of DMAC was added to the tube along with 100 μL of glacial $\text{CH}_3\text{CO}_2\text{H}$. It was noticed that although some fraction of the gel degraded, a significant portion remained intact even after 24 h. This suggested that the dynamic gel was at least partially converted to permanently crosslinked network. However, due to the moderate efficiency of radical coupling, and inconsistent curing throughout the gel, not all the dynamic linkages were converted to permanent

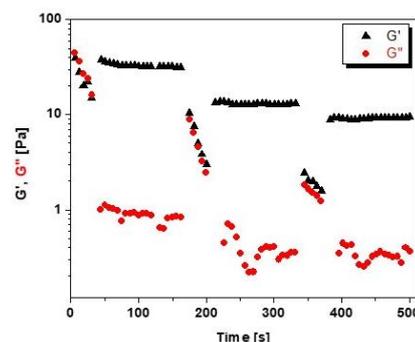


Fig. 5 Continuous step-strain measurement of the UV cured gel, in which, gel was subjected to 1300% strain for 30 s, then go back to 1% strain in the linear regime for 120 s, and 3 cycles were done.

bonds. In addition, transfer reactions to the solvent could have occurred. The gel was then washed again with DMAC until all the side products and extra Co Blue were removed. Then, 1 mL of DMAC was added, followed by 100 μL of glacial $\text{CH}_3\text{CO}_2\text{H}$ and the gel was left for 1 week. Even after that period, the gel did not degrade but swelled to a larger degree than the original dynamic precursor (Fig. 4d), owing to low crosslinking density after the curing. The main text of the article should appear here with headings as appropriate.

To confirm the formation of permanently crosslinked network, continuous step-strain measurements were carried out on the UV-light-cured gel. In this experiment, a dynamic gel was formed by mixing 400 μL of $\text{PhI}(\text{O}_2\text{CCH}_3)_2$ (0.15 M) solution with 1600 μL of $\text{Sty}_1\text{AA}_{0.7}$ (0.35 M) solution in DMAC. Subsequently, the gel was cured by using two UV lamps (254 nm, 21 W) for 90 min, followed by continuous step-strain measurement. The gel was subjected to high-amplitude oscillations ($\gamma = 1300\%$, $\omega = 10$ rad/s) for 30 s, resulting in an increase in the $\tan \delta$ value, which showed quasi-liquid-like behavior (Fig. 5). Moreover, G' did not recover to even close to its original value of 230 Pa. The average G' value measured under low amplitude oscillations ($\gamma = 1\%$, $\omega = 10$ rad/s) was only 33 Pa, which clearly suggested the scarcity of dynamic bonds, as expected. The data indicated that the major fraction of dynamic HV bonds were converted to permanent crosslinks (since the gel did not degrade in the presence of $\text{CH}_3\text{CO}_2\text{H}$). The self-healing efficiency was significantly decreased after the second and third cycle of high-amplitude oscillations due to unrecoverable damage to the dynamic bonds and crosslinked network during the first damage.

Similar conversion to permanent gel was achieved by microwave heating, but the gel was either completely degraded or not properly cured even after trying several different conditions. This is due to the high dielectric constant of DMAC,⁸¹ because of which, this medium attains high temperature even at low power of the microwave irradiation and in a short time. The steep increase in temperature did not provide sufficient time for the gel to set. Therefore, a lower dielectric constant solvent, 1,4-dioxane,⁸¹ was chosen, which proved to be optimal also because it dissolved well both $\text{PhI}(\text{O}_2\text{CCH}_3)_2$ and the Sty-AA copolymers, and swelled the final network polymer. The thermal curing of these gels was markedly improved compared

to similar systems using DMAc as the medium as shown in Fig. S4 (SI).

Although the conversion of dynamic into permanent networks has been reported previously,¹⁴ the approach presented here has the advantage of using readily accessible monomers and crosslinkers. In principle, any polymer containing carboxylate groups can be employed to prepare dynamic networks, which can be readily converted into permanent ones by simple irradiation or thermal treatment.

Conclusions

Dynamic gels were prepared using ligand exchange reaction between $\text{PhI}(\text{O}_2\text{CCH}_3)_2$ and the free pendant carboxylate groups in copolymers of Sty and AA. The gels exhibited self-healing, were confirmed by rheological measurements. The dynamic gel prepared by mixing 4:1 volume ratio $\text{Sty}_1\text{AA}_{0.7}$ (0.35 M) and $\text{PhI}(\text{O}_2\text{CCH}_3)_2$ (0.15 M) solutions in DMAc, respectively, showed 85% recovery even after 1300% strain in less than 20 s over several cycles. Furthermore, the conversion of dynamic to permanent gels following exposure to UV light or microwave heating was demonstrated. The conversion of dynamic gel to permanent crosslink network was visually confirmed by adding $\text{CH}_3\text{CO}_2\text{H}$ to the gel, which did not degrade the network even after a week. The formation of permanent gel was confirmed by continuous step-strain measurements, during which the gel showed poor recovery due to conversion of majority of dynamic bonds to permanent bonds by irreversible radical coupling reaction between the macromolecular carboxylate radicals and/or the alkyl radicals, which are product of their decarboxylation, produced by the photochemical or thermal cleavage of the (diacyloxyiodo)benzene bridging groups.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors gratefully acknowledge financial support provided by National Science Foundation (NSF Award Career 1455200). The authors also thank to Prof. Danieli Rodrigues and Mr. Danyal Siddiqui from University of Texas at Dallas for providing help with the rheological measurements.

References

- J. M. Lehn, *Proc. Natl. Acad. Sci. U.S.A.*, 2002, **99**, 4763-4768.
- J. R. Stuart, *Angew. Chem. Int. Ed.*, 2002, **41**, 899-952.
- J.-M. Lehn, *Aust. J. Chem.*, 2010, **63**, 611-623.
- D. Roy, J. N. Cambre and B. S. Sumerlin, *Prog. Polym. Sci.*, 2010, **35**, 278-301.
- M. A. C. Stuart, W. T. S. Huck, J. Genzer, M. Müller, C. Ober, M. Stamm, G. B. Sukhorukov, I. Szleifer, V. V. Tsukruk, M. Urban, F. Winnik, S. Zauscher, I. Luzinov and S. Minko, *Nat. Mater.*, 2010, **9**, 101.
- R. J. Wojtecki, M. A. Meador and S. J. Rowan, *Nat. Mater.*, 2011, **10**, 14-27.
- C. N. Bowman and C. J. Kloxin, *Angew. Chem. Int. Ed.*, 2012, **51**, 4272-4274.
- M. C. Stuparu, A. Khan and C. J. Hawker, *Polym. Chem.*, 2012, **3**, 3033-3044.
- J.-M. Lehn, *Angew. Chem. Int. Ed.*, 2013, **52**, 2836-2850.
- J.-M. Lehn, in *Hierarchical macromolecular structures : 60 years after the Staudinger Nobel Prize I*, ed. V. Percec, Springer, Cham ;, 2013, vol. 261, pp. 155-172.
- N. Roy, B. Bruchmann and J.-M. Lehn, *Chem. Soc. Rev.*, 2015, **44**, 3786-3807.
- W. L. A. Brooks and B. S. Sumerlin, *Chem. Rev.*, 2016, **116**, 1375-1397.
- B. V. K. J. Schmidt and C. Barner-Kowollik, *Angew. Chem. Int. Ed.*, 2017, **56**, 8350-8369.
- H. Sun, C. P. Kabb, Y. Dai, M. R. Hill, I. Ghiviriga, A. P. Bapat and B. S. Sumerlin, *Nat. Chem.*, 2017, **9**, 817.
- H. Frisch, D. E. Marschner, A. S. Goldmann and C. Barner-Kowollik, *Angew. Chem. Int. Ed.*, 2018, **57**, 2036-2045.
- F. García and M. M. J. Smulders, *J. Polym. Sci., Part A: Polym. Chem.*, 2016, **54**, 3551-3577.
- S. Ulrich, *Acc. Chem. Res.*, 2019, **52**, 510-519.
- Q. Zhang, C. Huang, F. Xia and J. Su, in *Electroactive Polymer (EAP) Actuators as Artificial Muscles: Reality, Potential, and Challenges*, ed. Y. Bar-Cohen, The Society of Photo-Optical Instrumentation Engineers, 2004, ch. 4, pp. 95-150.
- S. Burattini, B. W. Greenland, D. Chappell, H. M. Colquhoun and W. Hayes, *Chem. Soc. Rev.*, 2010, **39**, 1973-1985.
- E. B. Murphy and F. Wudl, *Prog. Polym. Sci.*, 2010, **35**, 223-251.
- S. Billiet, X. K. D. Hillewaere, R. F. A. Teixeira and F. E. Du Prez, *Macromol. Rapid Commun.*, 2012, **34**, 290-309.
- A. Phadke, C. Zhang, B. Arman, C.-C. Hsu, R. A. Mashelkar, A. K. Lele, M. J. Tauber, G. Arya and S. Varghese, *Proc. Natl. Acad. Sci. U.S.A.*, 2012, **109**, 4383.
- M. W. Urban, *Nat. Chem.*, 2012, **4**, 80-82.
- G. L. Fiore, S. J. Rowan and C. Weder, *Chem. Soc. Rev.*, 2013, **42**, 7278-7288.
- Z. Wei, J. H. Yang, J. Zhou, F. Xu, M. Zrínyi, P. H. Dussault, Y. Osada and Y. M. Chen, *Chem. Soc. Rev.*, 2014, **43**, 8114-8131.
- C. Barner-Kowollik and F. Georg Schmidt, *Macromol. Chem. Phys.*, 2012, **213**, 129-130.
- M. W. Urban, *Prog. Polym. Sci.*, 2015, **49-50**, 1-2.
- Y. Yang and M. W. Urban, *Adv. Mater. Interfaces*, 2018, **5**, 1800384-1800380.
- S. D. Bergman and F. Wudl, *J. Mater. Chem.*, 2008, **18**, 41-62.
- M. D. Hager, P. Greil, C. Leyens, S. van der Zwaag and U. S. Schubert, *Adv. Mater.*, 2010, **22**, 5424-5430.
- B. T. Michal, C. A. Jaye, E. J. Spencer and S. J. Rowan, *ACS Macro Lett.*, 2013, **2**, 694-699.
- Y. Yang and M. W. Urban, *Chem. Soc. Rev.*, 2013, **42**, 7446-7467.
- M. W. Urban, *Angew. Chem. Int. Ed.*, 2014, **53**, 3775-3775.
- Y. Yang, *Polym. Chem.*, 2013, **5**, 126-148.
- J. J. Cash, T. Kubo, A. P. Bapat and B. S. Sumerlin, *Macromolecules*, 2015, **48**, 2098-2106.
- Y. Yang, X. Ding and M. W. Urban, *Prog. Polym. Sci.*, 2015, **49-50**, 34-59.
- E. B. Stukalin, L.-H. Cai, N. A. Kumar, L. Leibler and M. Rubinstein, *Macromolecules*, 2013, **46**, 7525-7541.
- D. Y. Wu, S. Meure and D. Solomon, *Prog. Polym. Sci.*, 2008, **33**, 479-522.
- M. W. Urban, D. Davydovich, Y. Yang, T. Demir, Y. Zhang and L. Casabianca, *Science*, 2018, **362**, 220-225.

40. L. Voorhaar and R. Hoogenboom, *Chem. Soc. Rev.*, 2016, **45**, 4013-4031.
41. H. Jiang, L. Duan, X. Ren and G. Gao, *Eur. Polym. J.*, 2019, **112**, 660-669.
42. S. Datta, M. L. Saha and P. J. Stang, *Acc. Chem. Res.*, 2018, **51**, 2047-2063.
43. M. Enke, D. Döhler, S. Bode, W. H. Binder, M. D. Hager, U. S. Schubert and S. van der Zwaag, *Adv. Polym. Sci.*, 2016, **273**, 467-112.
44. M. Häring and D. D. Díaz, *Chem. Commun.*, 2016, **52**, 13068-13081.
45. L. Shi, P. Ding, Y. Wang, Y. Zhang, D. Ossipov and J. Hilborn, *Macromol. Rapid Commun.*, 2019, **40**, 1800837.
46. J. I. Musher, *Angew. Chem. Int. Ed.*, 1969, **8**, 54-68.
47. R. J. Hach and R. E. Rundle, *J. Am. Chem. Soc.*, 1951, **73**, 4321-4324.
48. G. C. Pimentel, *J. Chem. Phys.*, 1951, **19**, 446-448.
49. A. Yoshimura and V. V. Zhdankin, *Chem. Rev.*, 2016, **116**, 3328-3435.
50. G. Georgiev, E. Kamenska, L. Christov, I. Sideridou-Karayannidou, G. Karayannidis and A. Varvoglis, *Eur. Polym. J.*, 1992, **28**, 207-211.
51. A. Yoshimura, M. S. Yusubov and V. V. Zhdankin, *Org. Biomol. Chem.*, 2016, **14**, 4771-4781.
52. A. Maity and D. C. Powers, *Synlett*, 2019, **30**, 257-262.
53. J. V. Crivello, *Adv. Polym. Sci.*, 1984, **62**, 1-48.
54. J. V. Crivello, *J. Polym. Sci.*, 1999, **37**, 4241-4254.
55. A. Vaish and N. V. Tsarevsky, in *Main Group Strategies towards Functional Hybrid Materials*, eds. T. Baumgartner and F. Jaekle, Wiley, 2018, pp. 483-514.
56. G. Georgiev, S. Spyroudis and A. Varvoglis, *Polym. Bull.*, 1985, **14**, 523-526.
57. G. S. Georgiev, *Polym. Bull.*, 1999, **43**, 223-230.
58. G. S. Georgiev, E. B. Kamenska, N. V. Tsarevsky and L. K. Christov, *Polym. Int.*, 2001, **50**, 313-318.
59. R. Kumar, Y. Cao and N. V. Tsarevsky, *J. Org. Chem.*, 2017, **82**, 11806-11815.
60. A. Varvoglis, *Chem. Soc. Rev.*, 1981, **10**, 377-407.
61. R. Kumar, A. Vaish, T. Runčevski and N. V. Tsarevsky, *J. Org. Chem.*, 2018, **83**, 12496-12506.
62. K.-y. Akiba and Y. Yamamoto, *Heteroat. Chem.*, 2007, **18**, 161-175.
63. A. R. Fox and K. H. Pausacker, *J. Chem. Soc.*, 1957, DOI: 10.1039/jr9570000295, 295-301.
64. H. Han and N. V. Tsarevsky, *Polym. Chem.*, 2012, **3**, 1910-1917.
65. H. Han, R. Kumar and N. V. Tsarevsky, *Macromol. Rapid Commun.*, 2019, **40**, 1900073.
66. T. Muraki, H. Togo and M. Yokoyama, *Rev. Heteroatom Chem.*, 1997, **17**, 213-243.
67. H. Togo and M. Katohgi, *Synlett*, 2001, 565-581.
68. A. D. Asandei, O. I. Adebolu, C. P. Simpson and J.-S. Kim, *Angew. Chem. Int. Ed.*, 2013, **52**, 10027-10030.
69. G. Gody, D. A. Roberts, T. Maschmeyer and S. Perrier, *J. Am. Chem. Soc.*, 2016, **138**, 4061-4068.
70. A. Roy, in *Artists' Pigments: A Handbook of Their History and Characteristics*, ed. B. H. Berrie, National Gallery of Art, Washington, 2007, vol. 4, pp. 151-177.
71. G. Moad, J. Chiefari, Y. K. Chong, J. Krstina, R. T. A. Mayadunne, A. Postma, E. Rizzardo and S. H. Thang, *Polym. Int.*, 2000, **49**, 993-1001.
72. S. Perrier and P. Takolpuckdee, *J. Polym. Sci.: Part A: Polym. Chem.*, 2005, **43**, 5347-5393.
73. C. Barner-Kowollik, ed., *Handbook of RAFT Polymerization*, Wiley-VCH, Weinheim, 2008.
74. G. Moad, E. Rizzardo and S. H. Thang, in *Fundamentals of Controlled/Living Radical Polymerization*, eds. N. V. Tsarevsky and B. S. Sumerlin, RSC, Cambridge, 2013, ch. 6, pp. 205-249.
75. E. T. Denisov, T. G. Denisova and T. S. Pokidova, *Handbook of Free Radical Initiators*, Wiley, Hoboken, 2003.
76. F. Cech and E. Zbiral, *Tetrahedron*, 1975, **31**, 605-612.
77. N. V. Tsarevsky, *J. Polym. Sci.: Part A: Polym. Chem.*, 2010, **48**, 966-974.
78. S. Makowiec and J. Rachon, *Heteroat. Chem.*, 2003, **14**, 352-359.
79. A. Vaish, S. G. Roy and P. De, *Polymer*, 2015, **58**, 1-8.
80. M. T. Shaw, *Introduction to Polymer Rheology*, John Wiley & Sons, Incorporated, Hoboken, UNITED STATES, 2012.
81. C. Reichardt and T. Welton, in *Solvents and Solvent Effects in Organic Chemistry*, eds. C. Reichardt and T. Welton, Wiley, 2010, pp. 549-586.

Hypervalent Iodine-Based Dynamic and Self-Healing Network Polymers

Avichal Vaish and Nicolay V. Tsarevsky*

Department of Chemistry, Southern Methodist University, Dallas, TX, USA 75275

* Corresponding author. Phone: +1-214-768-3259; Email: nvt@smu.edu

