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One-pot blue-light triggered tough interpenetrating polymeric network (IPN) using CuAAC and methacrylate reactions

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Abstract

An interpenetrating polymeric network (IPN) is formed in a one-pot blue-light activated scheme, where the step- and chain- growth polymerizations of the CuAAC and methacrylate reactions, respectively, are simultaneously triggered but proceed sequentially. The glassy IPN is polymerized under ambient conditions and is able to withstand high strain before failure owing to its significantly enhanced toughness. Additionally, this material exhibits shape memory attributes with readily tunable mechanical properties at high temperature.

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An IPN is generated rapidly under blue-light in a one-pot scheme, forming a glassy and transparent material. The IPN exhibits high toughness and shape memory attributes.

Interpenetrating polymeric networks (IPNs) are an exclusive class of materials integrating two or more independent polymer networks that are interwoven but not covalently connected.^{1, 2} IPNs enable integration of various chemical functionalities, properties, and crosslinking chemistries from two or more networks to enhance the material performance.³ For example, the use of double networks in hydrogels has shown more than tenfold enhancement in strength over the constituent single networks.^{4, 5} Other examples have

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imparted antifouling and self-cleaning properties from one network to the other.^{6, 7} IPNs are used in an array of diverse commercial applications such as ion exchange resins, medical dressing, and automobile bumpers,⁸ and are typically synthesized by either a sequential or simultaneous method.¹ The sequential synthesis method, where a crosslinked network is swollen with a monomer that is further polymerized to form a second, interwoven network, enables integration of chemically incompatible monomers and crosslinkers. This method, however, suffers from being a diffusion limited (i.e., time-consuming) two-step process.⁹ The alternative, one-pot, simultaneous method has become the preferred route to synthesize IPNs, where the monomer precursors and crosslinkers for each network are present during network formation. The monomers must be miscible and possess orthogonal crosslinking functional groups that, upon reaction, form an independent, interwoven network or IPN.^{4, 10}

Recently, a number of researchers have exploited the orthogonal reactivity of click reactions to make IPNs via the simultaneous synthesis method,^{9, 11} such as IPN-based hydrogels, using the CuAAC and epoxy-amine reactions;¹² organogels, using the CuAAC and atom transfer radical polymerization (ATRP);¹³ and neat polymer networks, using Diels-Alder and urethane reactions.¹⁴ Although these systems are functional, they must be performed at elevated temperatures and/or over long time durations (50 °C/8 hrs, 60 °C/24 hrs, and 60 °C/30 mins, respectively). Moreover, while all of the mentioned examples are based on chemical orthogonality between functional groups, they lack non-thermal control over the reaction initiation.

Photoinitiation is a desired strategy for reaction control as it enables both spatio-temporal¹⁵ and wavelength control (photo-orthogonality).^{16, 17} Moreover, such reactions are often performed under ambient reaction conditions. In the case of IPNs, photopolymerization often exhibits higher reaction rates that mitigates phase separation, enabling higher degree of network interpenetration.^{8, 18} Although several sets of orthogonal chemistries can be implemented in a one-pot reaction scheme,^{11, 19–21} there are only a few that can be initiated using a single photoinitiator system.^{22–24} Most photoinitiated IPNs, such as the acrylate- and epoxy-based IPN, require two different initiating species (e.g., radicals for an acrylate reaction and cations for an epoxy reaction) and are sensitive to air.²⁵

In this communication, two orthogonal chemistries^{13, 26} in a one-pot reaction scheme are implemented with a single photoinitiating step to trigger the formation of two networks simultaneously and orthogonally at room temperature and in presence of air (Figure 1A). Specifically, we simultaneously photoinitiate CuAAC and methacrylate polymerizations using a single photoinitiator system. The photo-activated CuAAC (photo-CuAAC) reactions are resistant to oxygen inhibition and are typically initiated *in situ* by reduction of copper(II) to copper(I) using a photo-generated radical from a Norrish Type I (α -cleavage)^{15, 27} or Norrish Type II (electron-transfer)²⁸ photoinitiator. Similarly, methacrylate polymerizations can be initiated from photo-generated radicals.²⁹ Our synthetic one-pot IPN approach is initiated via blue-light irradiation (470 nm wavelength) of a Norrish Type II photoinitiating system comprised of camphorquinone and a tertiary amine (Figure 1B), which initiates both the CuAAC and methacrylate crosslinking reactions under ambient conditions.

A radical initiated methacrylate network formed via chain polymerization is well-known to possess heterogeneous network structure and brittle-like mechanical properties, whereas the step-polymerized CuAAC network is homogenous and tough.^{16, 30, 31} Herein, we investigate the structure-property relationship of chain- and step-polymerized entangled networks (i.e., methacrylate and CuAAC networks) using thermo-mechanical analysis of the IPN. We propose that the IPN formulation will overcome the brittle nature of methacrylate network, producing a toughened material that is effectively reinforced by the CuAAC network scaffold.

The extent of integration of IPN components often depends on the rate at which each individual network polymerizes.^{1, 32} In many cases, one of the polymerizing components will phase separate thwarting IPN formation; however, this can be mitigated if the polymerization rate is faster than the phase separation kinetics, where fast polymerization kinetics are often associated with higher interpenetration between networks.^{8, 18} The IPN formation kinetics are followed using real-time near infrared (NIR) spectroscopy, allowing the monitoring of independent functional groups. The Figure 2A shows the photopolymerization kinetics of network(s) formation in a 50–50 IPN [nomenclature representing 50:50 (wt/wt) CuAAC to methacrylate mixture, where the CuAAC component is a stoichiometrically balanced mixture of azide and alkyne monomers from monomers **1** and **2** (Figure 1C)]. Upon exposure to mild blue-light irradiation (470 nm wavelength at 30 mW cm⁻² intensity) under ambient conditions, the reactions do not initiate simultaneously and, surprisingly, the CuAAC reaction is initiated before methacrylate polymerization. Individually, the methacrylate polymerization starts instantly upon irradiation and reaches ~90% functional group conversion after 15 minutes and is more rapid than the CuAAC polymerization, which reaches ~85% functional group conversion after 30 minutes (Figure 2B). In contrast, the CuAAC reaction is first to initiate in the 50–50 IPN formulation, reaching >90% conversion in less than 10 minutes (Figure 2A). This observation is partially explained by the higher reactivity of the photo-induced radicals towards Cu(II)³³ species relative to the methacrylate double bond. Moreover, as the CuAAC network is formed, the unreacted methacrylate monomer act as a diluent imparting higher mobility and thus, an increased final conversion of CuAAC polymerization. The prolonged inhibitory period of the methacrylate in the IPN composition owes to the presence of copper cations which quench the excited triplet state of photoinitiator used here^{27, 34, 35} (Fig. S2 in SI showing the inhibitory effect of copper on the methacrylate polymerization in absence of the CuAAC monomers).²⁶ In the IPN, once the Cu(II) is depleted, the generated radicals overcome inhibition and the second methacrylate network begins polymerization after 5 minutes (Figure 2A). Additionally, the CuAAC cycloaddition reaction forms triazole rings, which has been show to ligate to the copper cations and may overcome photoinitiator excited state quenching by the Cu cation.³⁶ In the IPN, both the chemistries reach high conversions (above their individual network vitrification point), with a final CuAAC conversion of ~94% and a methacrylate conversion of ~87% in 15 minutes under irradiation.

The orthogonality of the CuAAC-methacrylate reaction during IPN polymerization is verified using FTIR spectroscopy (Fig. S4 in SI), which exhibits a one-to-one conversion profile throughout the reaction indicating minimal side reactions. While a loss in

orthogonality between azide and methacrylate groups for monofunctional reactants has been noted by Ladmiral et al.³⁷ at higher temperatures and longer reaction times, our photoinitiated approach enables rapid reaction under ambient conditions providing a route to form completely separate interwoven networks.^{13, 26} It is important to note that the use of a Norrish Type II photoinitiator system is critical for the development of distinct reaction stages. The use of Norrish Type I photoinitiators with the Cu(II) does not exhibit the inhibition effect on methacrylate polymerization under high or low intensity of light (Fig. S3 in SI). Upon five minutes of irradiation, the 50–50 IPN generates sufficient Cu(I) species capable of methacrylate conversion in dark (Fig. S5 in SI), similar to the controlled radical polymerization mechanism observed in ATRP reactions using redox mechanism between oxidation states of copper.^{26, 38} Additionally, it has been suggested that a faster step-growth polymerization followed by a subsequent chain-growth polymerization results in a regular underlying IPN cell structure, thereby increasing monomer dispersion, entanglements, and mitigating phase separations during the polymerization.^{8, 32} Herein, the CuAAC polymerization is first initiated and proceeds via a stepwise increase in the molecular weight which is associated with a delayed gel-point conversion relative to the methacrylate chain-growth polymerization that further reduces reaction diffusion limitations and enables the reaction to proceed to higher final conversions. The final one-pot IPN product is a glassy film that exhibits no phase separations as evident from its transparent appearance (inset Figure 2A).

The thermo-mechanical analysis of the glassy IPN films enables us to explore the properties and features imparted from each participating component within the IPN. The methacrylate polymerizes via a chain-growth mechanism and has a broad glass transition region arising from the heterogeneity in the network, as determined by the breadth in the $\tan(\delta)$ peak (Figure 3A).³⁹ The pure methacrylate network from monomer **4** has a broad glass transition region ($T_g \approx 126^\circ\text{C}$), whereas the pure CuAAC network, developed via a step-growth mechanism, is more homogenous with a lower and relatively narrower glass transition region ($T_g \approx 67^\circ\text{C}$).²⁸ For the IPN compositions, the prominent $\tan(\delta)$ peak associated with the glass transition temperature of CuAAC network is readily distinguished and invariant of methacrylate composition. The $\tan(\delta)$ peak height decreases with decreasing the CuAAC composition (i.e., from 100% CuAAC to 100% Methacrylate), which corresponds to the decrease mobilization of the CuAAC polymeric chains. The entanglements in IPN components acting as crosslinking points have previously shown a characteristic shift in the T_g of component networks in IPN compared with single networks, we also notice similar increase in T_g of CuAAC networks in IPN ($T_g \approx 71^\circ\text{C}$ in IPNs compared with $T_g \approx 67^\circ\text{C}$ in 100% CuAAC in Figure 3A).⁴⁰

The presence of step- and chain-polymerized networks in these glassy IPN materials provides a control handle over the modulus at higher temperature. In Figure 3B, the 100% CuAAC enters the rubbery regime at $\approx 80^\circ\text{C}$ with a modulus of $\approx 8.2\text{ MPa}$; at that same temperature, the 50–50 IPN has a storage modulus of $\approx 145\text{ MPa}$ which is ~ 8 times lower than 100% Methacrylate network possessing a modulus $\approx 1.13\text{ GPa}$. Thus, tunable mechanical properties at higher temperatures is achieved by simply adjusting the component

ratio in the network formulation, without affecting the glassy modulus of the material at the room temperature.

Although bulk methacrylate polymer networks are widely used in several applications, they suffer from being brittle.^{16, 30, 31, 41} The brittleness of the pure methacrylate network (i.e., 100% Methacrylate) is clearly evident in Figure 4A with a strain at break of $8.3 \pm 1.2\%$ in tension. In the IPN form, the brittle methacrylate network component is reinforced by the tough CuAAC component imparting the high toughness associated with it.^{39, 42} The pure CuAAC network (i.e., 100% CuAAC), which exhibits a glassy modulus at low strains, exhibits a high tensile toughness (Figure 4B),³⁰ and a maximum strain at break of $130 \pm 10\%$. It should be noted that the high strain tolerant behavior is observed to be age-dependent and the samples shown are tested in the same week after preparation. We speculate that the high strain tolerance owes to the presence of secondary interactions (π - π stacking and H-bonding) in the CuAAC network, however this effect and its time dependence requires further investigation.⁴³ The 50–50 IPN has a substantial increase in the strain at break ($40 \pm 3\%$) as compared with the pure methacrylate network, making these IPNs promising candidates to replace the brittle methacrylate films without compromising on the glassy modulus.⁴⁴

The shape of the IPN can be manipulated via deformation of the material below its T_g ; however, the material remembers its equilibrium state and will return to its original shape and dimension upon heating. The specimen deformed at ambient temperature retained its deformed shape, until it was thermally treated at 80°C for 15 minutes (Figure 4C). Typically, the reduction in T_g of glassy networks for such thermal shape memory is attained by the addition of small molecular weight plasticizer species or solvent, which are prone to leach from the network.^{31, 45} The brittle 100% Methacrylate network is incapable of withstanding even moderate flexural strain ($>8\%$) and fails during deformation. In contrast, the 100% CuAAC network possess high toughness and exhibits shape memory attributes upon heating above its T_g .⁴⁶ The IPNs described here exhibit shape retention property without any leachables, owing to the entanglement of the CuAAC and methacrylate networks.

In addition to shape memory, we demonstrate spatio-temporal control aspect of the 50–50 IPN via a simple photopolymerization using photomask transparency with excellent pattern fidelity (Figure 4D). This demonstration presents new opportunities for photolithographic applications of these flexural strain tolerant, shape retaining blue-light polymerized IPNs.⁴⁷

Conclusions

To conclude, a new blue-light triggered, solvent-free one-pot IPN synthetic strategy is demonstrated, which proceeds rapidly under ambient conditions and possesses ideal interpenetration between step- and chain-polymerized networks. The orthogonal chemistries used in this IPN, namely the CuAAC and methacrylate polymerizations, form interwoven networks triggered via light-activation of a Norrish Type II photoinitiating system. The inhibition of methacrylate polymerization, owing to the presence of copper cations, results in distinct step- and chain-growth polymerization reaction regimes, which facilitates high

functional group conversion (>90% within 15 minutes). The ability to photoinitiate this reaction enables spatio-temporal control over IPN fabrication, thus establishing this solvent-free strategy as a 'greener' alternative for many applications, including photolithographic resists, coatings, and medical implants. The thermo-mechanical properties of these glassy and transparent materials are tuned simply by adjusting the relative amounts of the two networks in the formulation. The IPNs exhibit shape memory, enhanced toughness, and high strain tolerances over the brittle methacrylate-based network owing to the entangled CuAAC network that acts as a 'non-leachable' additive. These attributes necessitate further investigation of the approach into solvated materials such as hydrogels and organogels, which are extensively utilized for drug delivery, ion-conductive membranes, and self-healing 3D printed networks.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Notes and references

1. Sperling, LH. Interpenetrating Polymer Networks. Vol. 239. American Chemical Society; 1994. p. 3-38.ch. 1
2. Gong JP. Science. 2014; 344:161. [PubMed: 24723604]
3. Lendlein A, Jiang H, Junger O, Langer R. Nature. 2005; 434:879–882. [PubMed: 15829960]
4. Gong JP, Katsuyama Y, Kurokawa T, Osada Y. Adv Mater. 2003; 15:1155–1158.
5. Chen Q, Chen H, Zhu L, Zheng J. Journal of Materials Chemistry B. 2015; 3:3654–3676.
6. Fei R, Means AK, Abraham AA, Locke AK, Côté GL, Grunlan MA. Macromolecular Materials and Engineering. 2016; 301:935–943. [PubMed: 28529447]
7. Dundua A, Franzka S, Ulbricht M. Macromol Rapid Commun. 2016; 37:2030–2036. [PubMed: 27778416]
8. Kim, SC., Sperling, LH. IPNs around the world : science and engineering. John Wiley, Chichester; New York: 1997.
9. Truong VX, Ablett MP, Richardson SM, Hoyland JA, Dove AP. J.Am.Chem.Soc. 2015; 137:1618–1622. [PubMed: 25590670]
10. Liu S, Dicker KT, Jia X. Chem.Commun. 2015; 51:5218–5237.
11. Gilbert T, Smeets NMB, Hoare T. ACS Macro Letters. 2015; 4:1104–1109.
12. Murakami T, Brown HR, Hawker CJ. Journal of Polymer Science Part A: Polymer Chemistry. 2016; 54:1459–1467.
13. Xu LQ, Yao F, Fu GD, Kang ET. Biomacromolecules. 2010; 11:1810–1817. [PubMed: 20518556]
14. Lyon GB, Baranek A, Bowman CN. Advanced Functional Materials. 2016; 26:1477–1485.
15. Adzima BJ, Tao Y, Kloxin CJ, DeForest CA, Anseth KS, Bowman CN. Nat Chem. 2011; 3:256–259. [PubMed: 21336334]
16. Bowman CN, Kloxin CJ. AIChE Journal. 2008; 54:2775–2795.
17. Chatani S, Kloxin CJ, Bowman CN. Polym.Chem. 2014; 5:2187–2201.
18. Athawale VD, Kolekar SL, Raut SS. Journal of Macromolecular Science, Part C. 2003; 43:1–26.
19. Xi WX, Scott TF, Kloxin CJ, Bowman CN. Advanced Functional Materials. 2014; 24:2572–2590.
20. Tunca U. Journal of Polymer Science Part A: Polymer Chemistry. 2014; 52:3147–3165.
21. DeForest CA, Polizzotti BD, Anseth KS. Nat Mater. 2009; 8:659–664. [PubMed: 19543279]

22. Sparks BJ, Hoff EFT, Hayes LP, Patton DL. *Chem.Mater.* 2012; 24:3633–3642.
23. Wang C, Podgorski M, Bowman CN. *Materials Horizons.* 2014; 1:535–539.
24. Blasco E, Wegener M, Barner-Kowollik C. *Adv Mater.* 2017
25. Xiao P, Dumur F, Graff B, Morlet-Savary F, Vidal L, Gigmes D, Fouassier JP, Lalevée J. *Macromolecules.* 2014; 47:26–34.
26. Geng J, Lindqvist J, Mantovani G, Haddleton DM. *Angewandte Chemie International Edition.* 2008; 47:4180–4183. [PubMed: 18412202]
27. El-Zaatari BM, Shete AU, Adzima BJ, Kloxin CJ. *Phys. Chem. Chem. Phys.* 2016; 18:25504–25511. [PubMed: 27711587]
28. Shete AU, El-Zaatari BM, French JM, Kloxin CJ. *Chem Commun (Camb).* 2016; 52:10574–10577. [PubMed: 27499057]
29. Roppolo I, Chiappone A, Angelini A, Stassi S, Frascella F, Pirri CF, Ricciardi C, Descrovi E. *Materials Horizons.* 2017
30. Tibbitt MW, Kloxin AM, Sawicki LA, Anseth KS. *Macromolecules.* 2013; 46:2785–2792.
31. Ligon-Auer SC, Schwentenwein M, Gorsche C, Stampfl J, Liska R. *Polym.Chem.* 2016; 7:257–286.
32. Sperling LH, Mishra V. *Polymers for Advanced Technologies.* 1996; 7:197–208.
33. Oz E, Uyar T, Esen H, Tasdelen MA. *Progress in Organic Coatings.* 2017; 105:252–257.
34. Marin ML, McGilvray KL, Scaiano JC. *J.Am.Chem.Soc.* 2008; 130:16572–16584. [PubMed: 19049456]
35. Scaiano JC, Stamplecoskie KG, Hallett-Tapley GL. *Chem.Comm.* 2012; 48:4798–4808.
36. Wang C, Wang D, Yu S, Cornilleau T, Ruiz J, Salmon L, Astruc D. *ACS Catalysis.* 2016; 6:5424–5431.
37. Ladmiral V, Legge TM, Zhao Y, Perrier S. *Macromolecules.* 2008; 41:6728–6732.
38. Stenzel MH, Barner-Kowollik C. *Materials Horizons.* 2016; 3:471–477.
39. Song HB, Sowen N, Shah PK, Baranek A, Flores A, Stansbury JW, Bowman CN. *Dental Materials.* 2016; 32:1332–1342. [PubMed: 27524230]
40. Hermant I, Damyaniidu M, Meyer GC. *Polymer.* 1983; 24:1419–1424.
41. Zhang Q, Fang Z, Cao Y, Du H, Wu H, Beuerman R, Chan-Park MB, Duan H, Xu R. *ACS Macro Letters.* 2012; 1:876–881.
42. Burattini S, Greenland BW, Merino DH, Weng W, Seppala J, Colquhoun HM, Hayes W, Mackay ME, Hamley IW, Rowan SJ. *J.Am.Chem.Soc.* 2010; 132:12051–12058. [PubMed: 20698543]
43. Baranek A, Song HB, McBride M, Finnegan P, Bowman CN. *Macromolecules.* 2016; 49:1191–1200. [PubMed: 27867223]
44. Wei W, Hu X, Qi X, Yu H, Liu Y, Li J, Zhang J, Dong W. *Colloids and Surfaces B: Biointerfaces.* 2015; 125:1–11. [PubMed: 25460596]
45. Ferracane JL. *Dental Materials.* 2006; 22:211–222. [PubMed: 16087225]
46. McBride MK, Gong T, Nair DP, Bowman CN. *Polymer.* 2014; 55:5880–5884. [PubMed: 25378717]
47. Mu X, Bertron T, Dunn C, Qiao H, Wu J, Zhao Z, Saldana C, Qi HJ. *Materials Horizons.* 2017

Figure 1.

(A) Interpenetrating polymeric network from blue-light contains networks from both a step-growth (CuAAC) and a chain-growth (methacrylate) reaction. (B) Photoinitiation mechanism using a camphorquinone-amine photosensitizing system. (C) Monomers and reagents used in this investigation: (1) bis(6-azidohexyl)(1,3-phenylenebis(propane-2,2-diyl))dicarbamate (azide), (2) 1-(prop-2-ynyloxy)-2,2-bis(prop-2-ynyloxymethyl)butane (alkyne), (3) Cu(II)-PMDETA (Cu(II)), (4) tetraethylene glycol dimethacrylate (methacrylate), (5) camphorquinone (CQ), and (6) 4,N,N-trimethyl aniline (amine).

Figure 2.

Polymerization kinetics monitored in (A) bulk photo-IPN and (B) separately polymerized network using real-time near infrared (NIR) spectroscopy. One-pot monomer formulation in (A) is 50–50 IPN resulting in a transparent film (inset). Functional group conversions are determined by monitoring the alkyne ($6540\text{--}6460\text{ cm}^{-1}$) and vinyl ($6200\text{--}6140\text{ cm}^{-1}$) groups for CuAAC and methacrylate reactions, respectively. All formulations are irradiated with 470 nm blue-light at 30 mW cm^{-2} after 1 minute in dark (marked by shaded region).

Figure 3.

Dynamic mechanical analysis (DMA) of polymerized IPN as a function of composition. (A) The glass transition (T_g) for each network is preserved as indicated by the invariance of the $\tan(\delta)$ peak location in (A), while the storage modulus as a function of temperature is readily tuned via a change in composition in (B). All specimens are 0.5 mm thick and irradiated for 20 minutes under 470 nm blue-light at 30 mW cm^{-2} intensity.

Figure 4.

(A) Increase in strain tolerance in IPN. (B) Tensile toughness comparison of separately polymerized networks with IPN. (C) Shape recovery in 50-50 IPN at 80 °C. (D) Photopatterning of 50-50 IPN sample with photomask shown as inset (scale bar = 4 mm). Specimen (A), (B) and (D) are 0.07 mm thick, while (C) is 0.5 mm thick, and all were irradiated for 20 minutes under 470 nm blue-light at 30 mW cm⁻² intensity.