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RESEARCH ARTICLE

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Charge transfer complexes as dual thermal/photo initiators for free-radical frontal polymerization

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Abstract

Frontal polymerization is a process in which a localized reaction zone propagates from the coupling of thermal transport and the Arrhenius rate dependence of an exothermic polymerization; monomer is converted into polymer as the front passes through an unstirred medium. Herein we report the first study of charge transfer complexes (CTCs) as photo/thermal initiators for free-radical frontal polymerization. Front velocity was studied as a function of mole ratio between an aromatic amine, such as dimethyl-p-toluidine or dimethylaniline, and an iodonium salt. It was found that the front velocity reached a maximum at a certain mole ratio of amine to iodonium salt. The velocity remained constant upon increasing the ratio of amine to iodonium salt past this critical ratio. Fronts were also studied using N-phenyl glycine as an electron donor, but its utility was limited by low solubility. Lastly, the steric and electronic effects of the iodonium salt and counter anion were explored. It was found that CTCs using iodonium salts with less nucleophilic anions gave higher front velocities. In terms of intrinsic reactivity, the CTC composed of N,N-dimethyl-p-toluidine and bis[4-(tert-butyl)phenyl]iodonium tetra(nonafluoro-tert-butoxy)aluminate gave the highest front velocity per molal of iodonium salt.

KEYWORDS

charge transfer complex, free-radical polymerization, frontal polymerization, photoinitiator, thermal initiator

1 | INTRODUCTION

Photopolymerization is a rapid process that uses less energy than thermal curing but is limited when it comes to the curing of thick and/or filled materials.[1–3] Frontal polymerization (FP) is a process that can combine the in-depth cure and curing of highly filled systems[4,5] offered by bulk polymerization with the high speed of photopolymerization.[6] Dual-cure initiators that can serve as both photo and thermal initiators for polymerization are of interest in the search for more energy-efficient methods of polymerization.[7–10]

Frontal polymerization was originally discovered by Chechilo and Enikolopyan in the 1970s[11–14] and then independently rediscovered by Pojman in the early 1990s.[15–21] Since its discovery, FP research has been extended to other areas such as deep eutectic solvents,[22–25] hydrogels,[26] ROMP,[27,28] gradient materials[29] and cationic-initiated polymerization.[30–35]

Charge transfer complexes (CTCs) are a potential replacement for peroxide-based initiators and have been shown to act as dual thermal and photoinitiators.[2,9,36–38] Charge transfer complexes (CTCs) are formed through the association of an electron donor with an electron acceptor. This interaction allows absorption of light in the visible range, which differs from the shorter absorption wavelengths of other photoinitiators such as iodonium salts. The absorption of longer wavelengths of light and the lack of peroxide and metals make CTCs an attractive alternative to traditional initiators.[3,39] A CTC is in equilibrium with its components, and this equilibrium is affected by both electronic and steric factors.[3] Various studies[40–42] have shown that charge transfer complexes can be used as thermal initiators, photoinitiators, and redox initiators for free-radical polymerization.

CTCs based on iodonium salts (the electron acceptor) and amines (the electron donor) can act as both thermal and photoinitiators for free radical and cationic polymerization. Garra et al. showed that CTCs based on iodonium salts and amines can be used as photoinitiators in a light-activated redox initiation system.[36] Polymerization in shadow areas is made possible through this combination of photoionization with redox initiation. A later study demonstrated that it is possible to cure extremely thick samples using iodonium/amine-based charge transfer complexes as photoinitiators, but cure speed and conversion decrease with depth.[43] The synthesis of filled materials also remains a challenge. Electron spin resonance studies by Garra et al.[36,44] demonstrated the formation of aryl radicals from CTCs based on iodonium salts and amines. Such studies explore the initiation potential of CTCs and give insight into the mechanism. Figure 1 shows the general reaction of CTC radical generation.

A study by Wang et al. demonstrated the steric and electronic effects of the amine on the formation of a charge-transfer complex using an iodonium salt.[37] Wang and coworkers later demonstrated the potential of phosphine, indole, and sulfonium-based CTCs.[9,38,45] Thus far, composite synthesis utilizing the dual-cure nature of charge transfer complexes has been limited to a combination of surface photocuring followed by thermal curing.[9] The dual initiating ability of CTCs is advantageous; however, the requirement of photocuring followed by bulk curing to manufacture composites remains a challenge. Current curing for such systems involves multiple passes for photocuring and several minutes or longer of bulk curing.[9,37,38,45]

This research explored the use of charge transfer complexes as dual thermal and photoinitiators for free-radical frontal polymerization. Combinations of various iodonium salts and amines were used to study their effects on front velocity. The electronic and steric effects of the CTC components were explored. The effect of the mole ratio between the amine and iodonium salt on front velocity is also shown.

2 | EXPERIMENTAL SECTION

2.1 | Materials

Trimethylolpropane triacrylate (TMPTA) was purchased from Allnex (Alpharetta, GA). N,N-dimethyl-p-toluidine (DMPT), bis(4-tert-butylphenyl)iodonium triflate (IOC-T), and bis(4-fluorophenyl)iodonium triflate (IOC-FT) were purchased from Sigma-Aldrich. Bis(4-tert-butylphenyl) iodonium hexafluorophosphate (IOC-P) and bis[4-(tert-butyl)phenyl]iodonium tetra(nonafluoro-tert-butoxy)aluminate (IOC-A) were purchased from TCI America (Portland, OR). p-(octyloxyphenyl)phenyliodonium hexafluoroantimonate (IOC-8) was purchased from Ambeed (Arlington Heights, Il). N-phenylglycine (NPG) and N,N-dimethylaniline (DMA) were purchased from Alfa Aesar. The chemical structures of the monomers and initiators are displayed in Figure 2.

2.2 | Mole ratio study

N,N-dimethyl-p-toluidine (DMPT) and N,N-dimethylaniline (DMA) were used as the electron-donating amines. p-(octyloxyphenyl)phenyliodonium hexafluoroantimonate (IOC-8) was used as the electron acceptor. The solubility of NPG is limited to 0.031 molal in the formulation, so fronts were studied using a CTC consisting of NPG and IOC-8 in a 1:1 mole ratio. To prepare the charge transfer complexes, 2 parts per hundred (phr) resin of IOC-8 was dissolved in TMPTA via sonication (30 min). Parts per hundred resin indicates the mass of material added per 100 g of resin. This amount of iodonium salt is equivalent to a concentration of 0.031 moles per kilogram. Various amounts of the amine donor were then added to form a CTC with a certain mole ratio of iodonium salt to amine. The resulting solutions were mixed and loaded into borosilicate glass tubes (16 × 150 mm). All fronts were initiated with either a soldering iron or a 395 nm LED gooseneck lamp from Prime LED CO LTD. with an intensity of 22 mW/cm^2. A video camera was used to monitor the front propagation, and the velocity was calculated by taking the slope of the position versus time plot. Each test tube was labeled with an adhesive measuring tape to record the position of the front. All experiments were performed in triplicate. To demonstrate the photoinitiation capabilities, the front of at least one replicate of each system was started by the LED lamp. A K-type

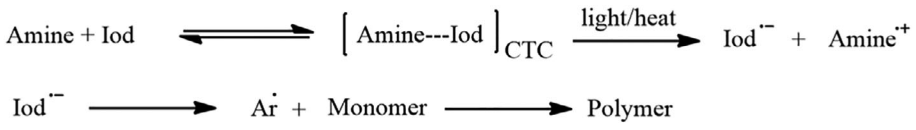

FIGURE 1 General reaction scheme for charge transfer complexe radical generation

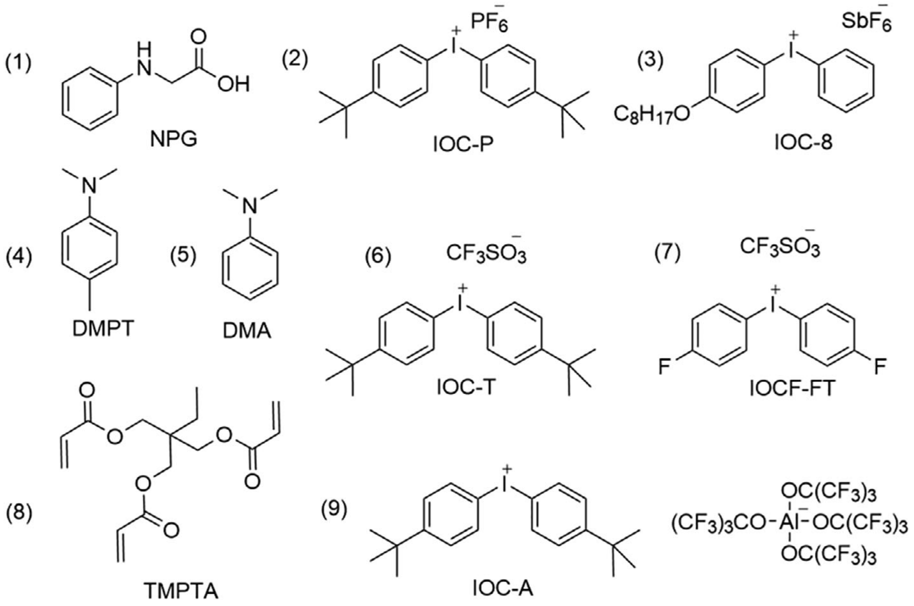

FIGURE 2 Chemical structures. Starting from the top row (from left to right): (1) N-phenylglycine (NPG), (2) bis(4-tert-butylphenyl)iodonium hexafluorophosphate (IOC-P), (3) p-(octyloxyphenyl)phenyliodonium hexafluoroantimonate (IOC-8), (4) dimethyl-p-toluidine (DMPT), (5) N,N-dimethylaniline (DMA), (6) bis (4-tert-butylphenyl)iodonium triflate (IOC-T), (7) bis(4-fluorophenyl) iodonium triflate (IOC-FT), (8) trimethylolpropane triacrylate (TMPTA), and (9) bis[4-(tert-butyl) phenyl]iodonium tetra(nonafluoro-tert-butoxy)aluminate (IOC-A)

thermocouple was used in one of the trials involving the 3:1 DMA:IOC-8 and 3:1 DMPT:IOC-8 CTC formulations to measure the front temperature of these systems. The thermocouple was placed in the center of the test tube at approximately half the depth of the solution.

2.3 | Iodonium salt

A constant amount of iodonium salt was mixed with DMPT in a 5:1 mole ratio. IOC-8, IOC-P, IOC-A, IOC-T, and IOC-FT were all tested as iodonium salts. Two different amounts of iodonium salt (1 or 2 phr) were added due to the limited solubility of IOC-FT. Because the iodonium salts were kept at a constant mass, the front velocities were converted into front velocity/molal of iodonium salt to elucidate the effect of changing the iodonium salt on the intrinsic reactivity of the system. As shown in Equation (1), This conversion is done by dividing the front velocity by the molality of the given iodonium salt. The resulting units are cm/min*kg/mol.

$$\frac{\text{Front velocity (cm/min)}}{\text{Molality}\left(\frac{\text{mol of iod}}{\text{kg of TMPTA}}\right)} = \frac{\text{cm}}{\text{min}} \times \frac{\text{kg of TMPTA}}{\text{mol of Iod}} = \frac{\text{cm}}{\text{min}} \times \frac{\text{kg}}{\text{mol}}. \quad (1)$$

2.4 | Pot life

To study the pot life, one sample of each formulation was wrapped in aluminum foil to prevent light penetration, and another sample was exposed to the ambient light of the lab. The formulations were checked at least every few days to determine if gelation occurred.

3 | RESULTS AND DISCUSSION

3.1 | Mole ratio study

Figure 3 shows the plot of front velocity vs. the mole ratio of DMPT to IOC-8. A front could not be obtained with IOC-8 alone, and the front was quenched in the formulation with the 1:4 mole ratio. This shows that the formation of the CTC is necessary for frontal polymerization. The front velocity initially increased as more amine was added and then reached a maximum velocity after the 2:1 mole ratio was reached. The minimum mole ratio detected for a self-sustaining front was 1:2 DMPT to IOC-8. Photopolymerization kinetic studies by Ghosh and co-workers showed that the polymerization rate reaches a maximum at a 2:1 mole ratio of electron donor to electron acceptor.[40,41] Their studies involved CTCs based on morpholine and sulfur dioxide/bromine as electron donors. The researchers concluded that the full complexation of the electron donor and acceptor occurred at this ratio.[40,41] Front velocity is a function of the polymerization rate, so the trends are comparable. In addition, morpholine has two available electron donor groups, one for each electron acceptor. In this work, the iodonium salts and amines each have one accepting and donating group, respectively.

As shown in Figure 4, the effect of the mole ratio of DMA to IOC-8 was studied in the same fashion as with DMPT. First, a 1:1 mole ratio system was tested; however,

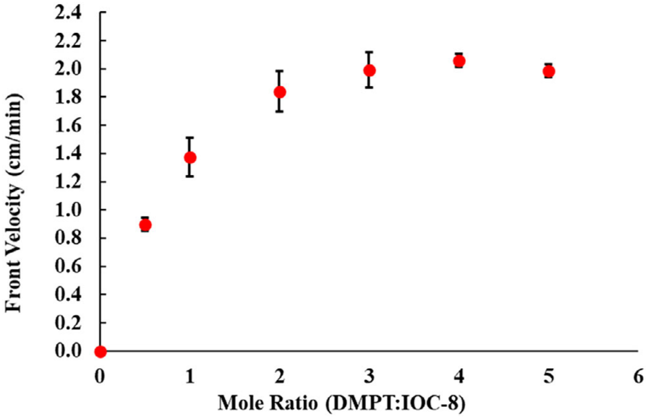

FIGURE 3 Effect of mole ratio (DMPT: IOC-8) on front velocity. The IOC-8 concentration was kept constant (0.031 molal)

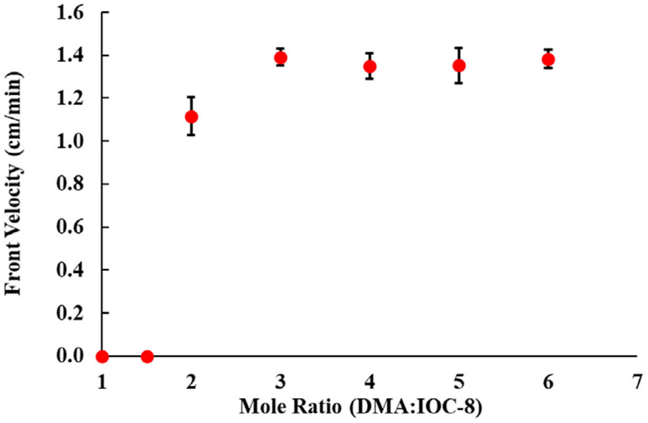

FIGURE 4 The effect of mole ratio (N,N-dimethylaniline (DMA):p-(octyloxyphenyl)phenyliodonium hexafluoroantimonate (IOC-8)) on front velocity. The concentration of IOC-8 was kept constant (0.031 molal)

a self-sustaining front could not be initiated. Next, a 1.5:1 mole ratio was attempted, and a front could not be sustained. Finally, a 2:1 mole ratio was attempted, and an average front velocity of 1.1 cm/min was obtained. This maximum velocity is significantly lower than the 2.0 cm/min for the 2:1 mole ratio formulation containing DMPT and IOC-8. The lower maximum velocity and the higher mole ratio of amine to iodonium salt required to reach a maximum constant velocity using DMA in comparison to DMPT indicate that the system is less reactive. The lower reactivity can be attributed to DMPT being a better electron donor than DMA because of the electron-donating methyl group in the para position. Front temperatures of 226 and 232°C were recorded for the 3:1 DMPT:IOC-8 and 3:1 DMA:IOC-8 CTCs, respectively. These values are typical for frontal polymerization.

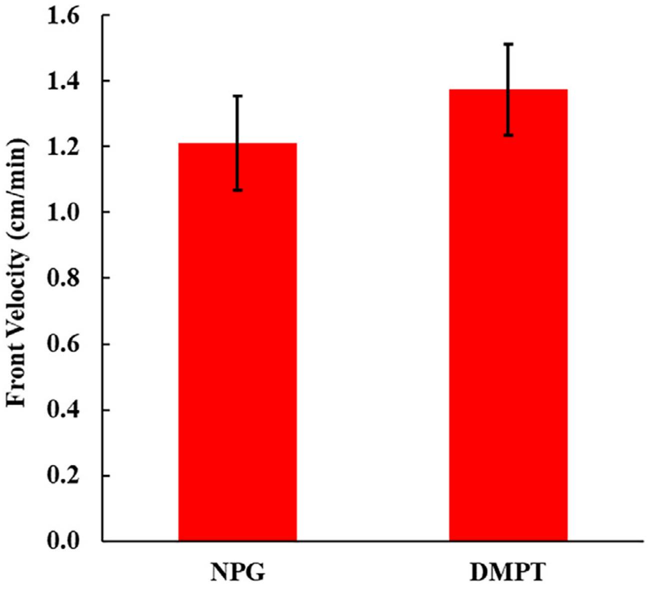

FIGURE 5 Comparison of front velocity between N-phenylglycine and N,N-dimethyl-p-toluidine charge transfer complex (CTC). Each CTC contains 2 phr of p-(octyloxyphenyl) phenyliodonium hexafluoroantimonate (IOC-8) (0.031 molal)

It can be concluded that complete conversion of the amine and iodonium salt to the CTC is reached at a 2:1 ratio for the DMPT:IOC-8 system and a 3:1 ratio for the DMA:IOC-8 system. The CTC formed between DMPT and IOC-8 has a higher equilibrium constant compared to the one formed between DMA and IOC-8, and additional DMA is needed to reach maximum complexation. Upon reaching complete complexation, the velocity remained constant despite the addition of more amine.

A CTC made from a 1:1 mole ratio of NPG:IOC-8 was also prepared, and its front velocity is compared to that of the 1:1 mole ratio of DMPT:IOC-8 in Figure 3. A mole ratio study with NPG was not done because in combination with IOC-8, the NGP was insoluble at concentrations beyond 0.0301 molal.The results of this study, shown in Figure 5, reveal that no significant difference in front velocity was found between fronts initiated by either NPG or DMPT based CTCs. The two formulations contained equal molar amounts of the amine (NPG or DMPT) and IOC-8, which suggests that the two CTCs have similar reactivity about initiating polymerization.

3.2 | Structure and counterion effects of iodonium salt on front velocity

Figures 6 and 7 show the front velocity for systems with the same mass of iodonium salt combined with DMPT in a 5:1 DMPT to IOC mole ratio. Figure 6 demonstrates that the formulations with IOC-P and IOC-8 gave the highest front velocities while the formulation with the IOC-A gave the lowest. Figure 7 shows that the IOC-8, IOC-FT, and IOC-P systems have similar front velocities while those with IOC-T are significantly lower.

On a mass basis, it appears that IOC-8 and IOC-P are more efficient as the electron acceptors in comparison to IOC-A and the triflate iodonium salts. However, the intrinsic reactivity of the iodonium salts in the CTCs must be judged based on concentration. The data for Figures 8 and 9 were obtained by dividing the front velocity data in Figures 6 and 7 by the molality of the given iodonium salt. Figures 8 and 9 show these systems with a plot of front velocity per molal of iodonium salt. Based on intrinsic reactivity, the CTC with IOC-A gave the highest front velocities. The only difference between IOC-P and IOC-A is the counterion.

Klikovits showed that IOC-A is a more highly reactive photoacid generator in comparison to other iodonium salts.[46] Based on previous work by Krossing et al., it was proposed that the low nucleophilicity of the aluminate ion prevents it from recombining with the propagating cation.[47] Further work by Knaack et al. found that radical-induced cationic fronts initiated using IOC-A gave higher front velocities in comparison to those initiated by IOC-8.[48] The system in this study is based on free radicals so this does not explain the observed result. Counter anions with lower nucleophilicity are less tightly bound to the cation, in this case, the iodonium salt.[3] The PF_6^- and SbF_6^- anions of IOC-P and IOC-8, respectively, are more nucleophilic and more tightly bound to the iodonium when compared to the aluminate counter anion. Because the iodonium salt of IOC-A is less tightly bound to the counter anion, it is easier for it to interact with an electron donor such as DMPT to form a charge transfer complex.

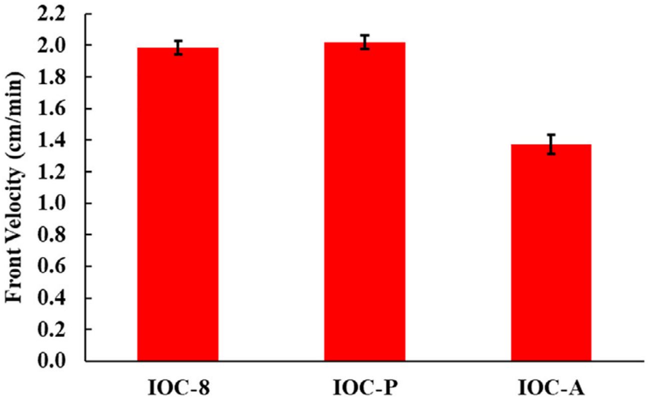

FIGURE 6 Front velocity for charge transfer complexes composed of various iodonium salts (2 phr) mixed with N,N-dimethyl-p-toluidine in a 5:1 mole ratio

The reason for the difference in front velocity between IOC-8 and IOC-P is more difficult to elucidate because both counter anions are different along with the structure of the iodonium salt. Nevertheless, the higher nucleophilicity of PF_6^- relative to SbF_6^- is at least partly responsible since the ion pair in IOC-P will be more tightly bound relative to IOC-8. It is also possible that the presence of the two tert-butyl groups in IOC-P are increasing steric effects and further hindering CTC formation.

Figure 9 demonstrates that IOC-8 is more reactive than the triflate containing iodonium salts. The lower reactivity of the triflate salts is likely due to the stronger binding of the triflate to the iodonium salt. Triflate is more nucleophilic in comparison to PF_6^- and SbF_6^- and therefore will be more tightly bound to the iodonium salt.[3] The higher reactivity of IOC-FT in comparison to IOC-T can be explained by the presence of fluorine

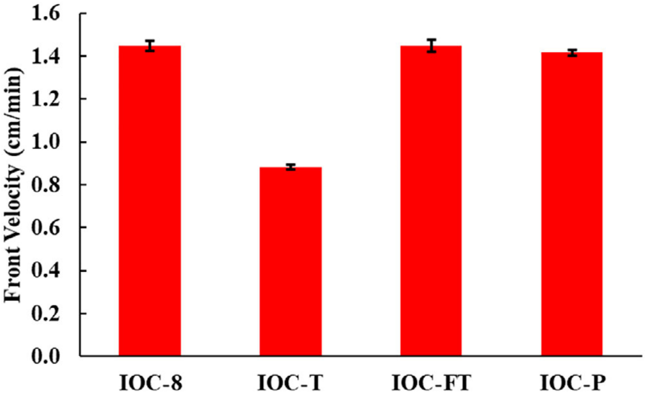

FIGURE 7 Front velocity data for charge transfer complexes composed of various iodonium salts (1 phr) mixed with N,N-dimethyl-p-toluidine in a 5:1 mole ratio

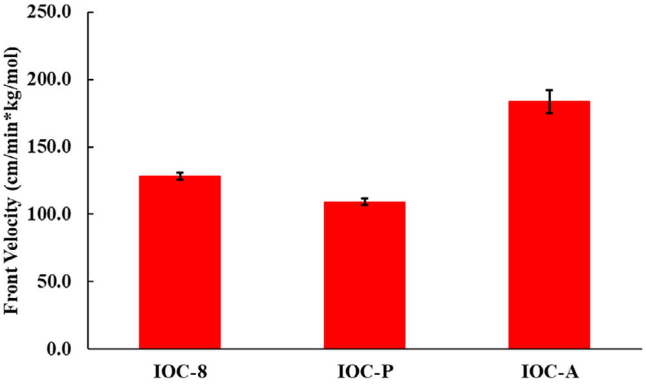

FIGURE 8 Data showing the front velocity per molal of iodonium salt for charge transfer complexes composed of various iodonium salts (2 phr) mixed with N,N-dimethyl-p-toluidine in a 5:1 mole ratio

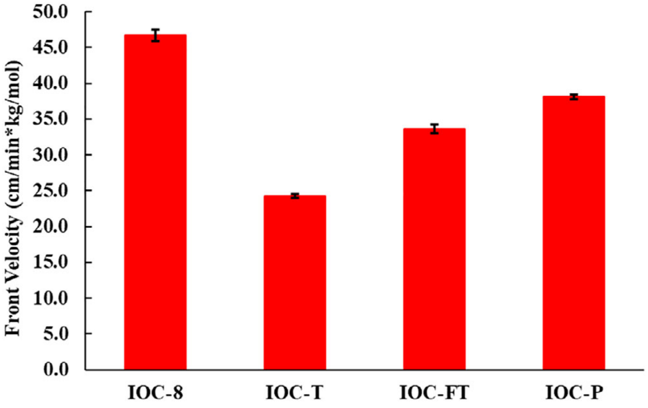

FIGURE 9 Data showing the front velocity per molal of iodonium salt for charge transfer complexes composed of various iodonium salts (1 phr) mixed with N,N-dimethyl-p-toluidine in a 5:1 mole ratio

groups on the latter. IOC-FT is a better electron acceptor due to the enhanced electron withdrawing of fluorine relative to the tert-butyl groups. Garra et al. found similar results through UV–Vis spectroscopy and computational simulations of CTCs formed using IOC-T, IOC-FT, and IOC-P.[43] The increased steric hindrance because of the two tert-butyl groups may also hinder CTC formation between IOC-T and DMPT.

3.3 | Pot-life study

In addition to the higher reactivity of DMPT, there was no apparent change in viscosity or gelation for the 1:2 and 1:1 mole ratio sample left unwrapped in glass vials for 2 months; gelation started after 2 months. Samples wrapped in foil and not exposed to light have yet to show any apparent changes in viscosity after 5 months.

4 | CONCLUSIONS

The first use of charge transfer complexes as initiators for free-radical frontal polymerization was demonstrated. CTCs were prepared by mixing various iodonium salts and amines in the bulk resin. Different iodonium salts and amines were used to study their structural and electronic effects on front velocity. A study on the effect of the mole ratio of amine to iodonium salt was done using DMPT, DMA, and IOC-8. Both front velocity and velocity per molal of iodonium salt were plotted to show both the practical applications of CTCs as initiators for fronts as well as the intrinsic reactivity.

It was found that CTCs using DMPT as the electron donor gave higher front velocities in comparison to those with DMA-based CTCs. This demonstrated that stronger electron-donating amines are more favorable towards CTC formation. Optimal ratios of amine and iodonium salt were found: 2:1 for DMPT:IOC-8 and 3:1 for DMA: IOC-8. Upon reaching these ratios, the front velocity reaches a maximum velocity despite the addition of more amine. It was concluded that the front velocity reaches a maximum upon maximum complexation of the amine and iodonium salt.

The studies involving changing the counter anion of the iodonium salt reveal that a combination of steric effect and nucleophilicity affects the front velocity. Both triflate-based CTCs gave lower front velocity than CTCs with IOC-8 and IOC-P. The lower velocities can be attributed to the triflate binding more tightly to the iodonium in comparison to the less nucleophilic SBF_6^- and PF_6^- anions. The difference in front velocities per molal between the two triflate iodonium salts revealed that the addition of electron-withdrawing groups on the iodonium salt increases front velocity by enhancing the CTC reactivity. IOC-A and DMPT form the most reactive CTCs, however, CTCs composed of IOC-8 and DMPT are the most useful in terms of costs while maximizing the front velocity and solubility.

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AUTHOR CONTRIBUTIONS

Daniel Gary: Conceptualization (lead); formal analysis (lead); investigation (lead); methodology (lead); writing – original draft (lead); writing – review and editing (equal). **Douglas Ngo:** Investigation (supporting). **Amber Bui:** Investigation (supporting). **John A. Pojman:** Formal analysis (supporting); writing – review and editing (equal).

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