

HIGH-POWER NIR-LED INDUCED CATIONIC AND RADICAL/CATIONIC HYBRID PHOTOPOLYMERIZATION

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The combinational NIR initiating system comprised heptamethine cyanine as sensitizer and iodonium salt as co-initiator exhibited excellent reactivity to initiate the cationic polymerization of epoxides, vinyl ether and oxetane upon the high power NIR-LEDs. The influence of the anions, which were selected from fluorinated phosphates (**a**: $[\text{PF}_6]^-$, **b**: $[\text{PF}_3(\text{C}_2\text{F}_5)_3]$, **c**: $[\text{PF}_3(n\text{-C}_4\text{F}_9)_3]$), aluminates (**d**: $[\text{Al}(\text{O-}t\text{-C}_4\text{F}_9)_4]^-$, **e**: $[\text{Al}(\text{O-}(i\text{-C}_3\text{F}_7)\text{CH}_3)_4]^-$), and methide $[\text{C}(\text{O-SO}_2\text{CF}_3)_3]^-$ (**f**) and carried by sensitizer and iodonium salt, to the reactivity of the combinational initiating system was studied. The NIR initiating system comprising aluminate anion **d** $[\text{Al}(\text{O-}t\text{-C}_4\text{F}_9)_4]^-$ showed the best performance. The system comprising fluorinated phosphate anion **b** exhibited better performance following **d**, and both of the anions were introduced as alternatives to **a**, because **a** easily caused HF issue in practical applications. Density functional theory calculations offered a rough pattern regarding the electrostatic potential of each anion where **d** showed a rather better performance compared to **e**. The more efficient shielding of all CF_3 - groups can explain these findings. Additionally, the conjugate acid generation study showed that the NIR initiating system comprising aluminate anion **d** generated the most amount of conjugate acid, which also could partly interpret its best performance to initiate the cationic polymerization. Furthermore, the interpenetrating polymer networks (IPNs) carrying one phase was firstly synthesized using trimethylpropane triacrylate (TMPTA) and **3,4-Epoxy cyclohexanemethyl 3,4-epoxycyclohexanecarboxylate (ERL-4211)** as monomer (Wt/Wt: 1:1) and NIR combinational initiating system comprising aluminate anion **d** by NIR-LED induced free radical/cationic hybrid photopolymerization meanwhile the UV-LED initiation using the same monomers but the photo-initiating system comprised of thioxanthone/iodonium salt failed to get one phase of IPNs. Exposure was carried out with new NIR-LED devices emitting at either 805 nm or 870 nm with intensity at around $1\text{W}/\text{cm}^2$. [1]

[1] Y. Pang, A. Shiraishi, D. Keil, S. Popov, V. Strehmel, H. Jiao, J. S. Gutmann, Y. Zou, B. Strehmel, "NIR-Sensitized Cationic and Hybrid Radical/Cationic Polymerization and Crosslinking" *Angew. Chem., Int. Ed.* 2021, 60, 1465-1473.