Rapid Report Photoinitiated radical polymerization using charge transfer complex of *N*-ethoxy-*p*-cyanopyridinium salt and 1,2,4-trimethoxybenzene

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Photoinitiated polymerization has gained much attention during the last two decades due to its application in various industrial areas.¹ In such applications both free radical² and cationic photoinitiated polymerizations³ have been used and the mechanisms of initiation have been studied in detail. Aromatic carbonyl compounds are the most widely used initiators for free radical polymerization of vinyl monomers.¹ As depicted in reaction (1) for benzoin derivatives,⁴ upon photolysis they undergo α -cleavage to produce the corresponding radicals.

$$\underbrace{\bigcirc}_{\mathsf{OR}^1}^{\mathsf{R}^2} \underbrace{\longrightarrow}_{\mathsf{OR}^1}^{\mathsf{hv}} \underbrace{\bigcirc}_{\mathsf{OR}^1}^{\mathsf{hv}} \underbrace{\bigcirc}_{\mathsf{OR}^1}^{\mathsf{R}^2} \underbrace{\bigcirc}_{\mathsf{OR}^1}^{\mathsf{R}^2} (1)$$

Initiators exhibiting such cleavage with high quantum efficiency show low absorption at wavelengths greater than 350 nm and their use is limited, particularly in pigmented coatings. Acylphospine oxides, ^{5,6} especially bisacylphosphine oxides, dyecoinitiator systems² and titanocene type initiators⁷ are known as long wavelength initiators.

Recently, we have shown that alkoxy pyridinium salts can act directly or indirectly as photoinitiators for cationic polymerization of appropriate monomers such as cyclic ethers and vinyl ethers.⁸ More recently, it was demonstrated⁹ that charge transfer complexes, formed by mixing certain pyridinium ions with aromatic electron donors, act as photoinitiators for cationic polymerization. It was suggested that radical cations of donors, formed by excitation of charge transfer (CT) complexes according to the mechanism in reactions (2) and (3), initiate polymerization.

Alkoxy pyridinium salts, in conjunction with photosensitizers such as anthracene, can also be



used¹⁰ in photoinitiated free radical polymerization. In this case, ethoxy radicals formed by electron transfer initiate polymerization (reactions (4) and (5)).



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