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Notes

Photoinitiated Zwitterionic Polymerization of Alkyl Cyanoacrylates by Pyridinium Salts

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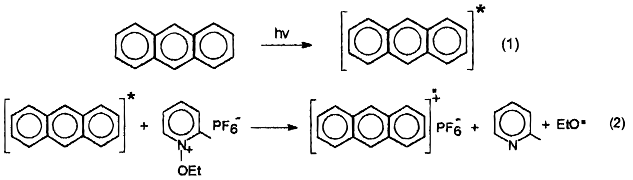
In recent years, photopolymerization has attracted much attention because of its increasing technical importance in various applications.[1] Much effort has been devoted to free-radical photoinitiated polymerization, mainly due to the availability of a wide range of photoinitiators.[2] Since the discovery of onium salt photoinitiators,[3] namely, iodonium and triarylsulfonium salts, the photoinitiation of cationic polymerization has also been the subject of intense investigation. However, only a few attempts have been made on the anionic counterpart. Fukuchi et al.[4] reported the anionic coordination polymerization of epoxides by a new catalyst system consisting of titanium tetraisopropoxide and photochemically generated phenol. Recently, photoinitiated anionic polymerization of cyanoacrylates has been reported.[5] It was claimed that isocyanate ions, generated by ligand exchange reaction upon photolysis, were the initiating species. Alkyl cyanoacrylates undergo anionic polymerization in the presence of a tertiary amine compound such as pyridine.[6] The polymerization proceeds via a zwitterionic mechanism. Kutal and co-workers[7] reported the use of $Pt(acac)_2$ complex in photoinitiated anionic polymerization of ethyl cyanoacrylate (ECA). Initiating species were claimed to be free acetylacetonate anions produced by the photoexcitation of the complex. Quite recently, *N*-alkoxypyridinium and *N*-isoquinolinium salts have been shown to act as photoinitiators for cationic[8] and free-radical polymerization.[9] Besides direct activation, their spectral response may be extended to longer wavelengths by the utilization of free-radical photoinitiators,[10−12] photosensitizers,[13] and charge transfer complexes.[14] In the case of photosensitized systems, it has been suggested and confirmed[13] by laser flash photolysis that the sensitized photolysis of *N*-alkoxypyridinium ions leads to the formation of photosensitizer radical cations capable of initiating cationic polymerization of related monomers. This is illustrated for the case of anthracene-sensitized photodecomposition of the *N*-ethoxy-2-methylpyridinium ions (EMP^+) by reactions 1 and 2.

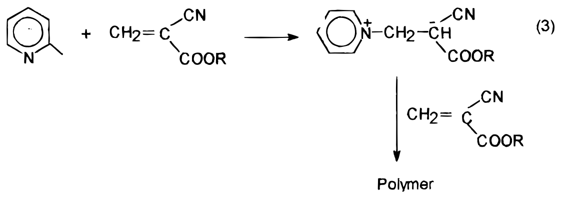
It appears feasible that 2-picoline formed concomitantly is capable of initiating the zwitterionic polymerization of alkyl cyanoacrylates and that, therefore, pyridinium salts might also be used as photoinitiators for anionic polymerization.



A representative procedure for the photoinitiated polymerization is as follows. A solution of ethyl cyanoacrylate (ECA) (4.41 mol L^{-1}) containing EMP^+ (1×10^{-2} mol L^{-1}), hydroquinone (2×10^{-2} mol L^{-1}), and anthracene (2.8×10^{-2} mol L^{-1}) was degassed with nitrogen and then irradiated in a photoreactor equipped with 15 Philips lamps emitting nominally at $\lambda = 350$ nm. Light intensity was measured by an Aberchrome actinometer and found to be 6.12×10^{-5} einstein s^{-1}. After 90 min of irradiation, a significant viscosity increase was observed. The polymer was then obtained by adding excess methanol containing a small amount of acid, and conversion was determined gravimetrically. Notably, solutions of ECA containing only anthracene undergo no change in viscosity when irradiated for the same time (Table 1). Further experiments have been performed to see the effect of methanesulfonic acid on our system. It was observed that addition of methanesulfonic acid from 10 to 100 ppm inhibits the polymerization of ECA.

Initiation by ethoxy radicals, which are also formed, occurs only to a negligible extent since the sample containing hydroquinone as a radical scavenger resulted in no change in the yield. Moreover, the formation of 2-picoline during the photolysis of acetonitrile solution of EMP^+, anthracene, and hydroquinone was detected by high-pressure liquid chromatography (HPLC).

The chemistry of initiation is expected to be identical to that described[15] for deliberately added amines, which involves addition to the monomer, thus forming zwitterionic species as depicted below.



In summary, it was demonstrated that the irradiation of ECA containing anthracene and EMP^+ in CH_2Cl_2 initiates anionic polymerization. The initiation step involves addition of photoreleased 2-picoline to the carbon−carbon double bond of the acrylate monomer. Previous studies and this work reveal that *N*-alkoxypyridinium salts are useful photoinitiators for all types of chain polymerization, i.e. cationic, free-radical, and anionic polymerization. Further studies are now in progress.

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Henkel (Sichel) Co. for providing ethyl cyanoacrylate.

Table 1. Photoinitiated Polymerization[a] of Ethyl Cyanoacrylate

run	anthracene (mol L^{-1})	EMP$^+$ (mol L^{-1})	hydroquinone (mol L^{-1})	conv (%)	M_n (g mol^{-1})
1	2.8×10^{-2}	1×10^{-2}		100	27600
2	2.8×10^{-2}	1×10^{-2}	2×10^{-2}	100	18700
3	2.8×10^{-2}		2×10^{-2}	0	

[a] [ECA] = 4.41 mol L^{-1}, time = 90 min, $\lambda = 350$ nm, $I = 6.12 \times 10^{-5}$ einstein s^{-1}.

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