Die Angewandte Makromolekulare Chemie **264** *(1999) 56–59 (Nr. 4596)*

Photoinitiated polymerization of ethyl cyanoacrylate by phosphonium salts

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(Received 20 July 1998)

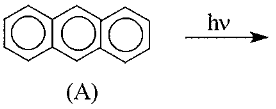
SUMMARY: The photoinitiated polymerization of ethyl cyanoacrylate (ECA) by benzyl triphenylphosphonium hexafluoroantimonate (BP^+) and (anthracen-9-ylmethyl)triphenylphosphonium hexafluoroantimonate (MAP^+) was studied. Zwitterionic and free radical mechanisms which involved homolytic and heterolytic decomposition of the phosphonium salts are discussed. The anthracene-sensitized photopolymerization of ECA was also demonstrated.

ZUSAMMENFASSUNG: Die photoinitiierte Polymerisation von Cyanacrylsäureethylester (ECA) mit Benzyltriphenylphosphoniumhexafluorantimonat (BP^+) und (Anthracen-9-ylmethyl)triphenylphosphoniumhexafluorantimonat (MAP^+) als Photoinitiatoren wurde untersucht. Ein zwitterionischer sowie ein radikalischer Mechanisms, einschließlich der homolytischen und heterolytischen Zersetzung der Phosphoniumsalze, werden diskutiert. Die mit Anthracen initiierte Photopolymerisation von ECA wurde ebenfalls untersucht.

Introduction

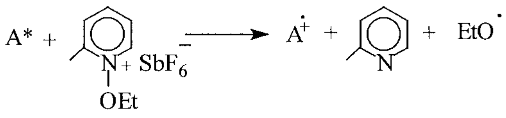
Photopolymerization of various monomers is gaining increasing importance in the field of polymer material science. For example, polymeric coatings with desired thickness and physical and mechanical properties can essentially be prepared by photopolymerization of appropriate formulations containing monomers, initiators and additives via free radical or cationic routes1). Free radical polymerization of acrylate and methacrylate-based monomers have been investigated in detail with a wide variety of photoinitiators and the chemistry involved is now well established.

During the past two decades considerable attention has also focused on technically applied cationic photopolymerizations involving vinyl ethers and epoxides as monomers2). The major classes of photoinitiators which can successfully be applied to initiate cationic polymerization include diaryl iodonium3), triaryl sulfonium4) and *N*-alkoxy pyridinium salts5), and iron arene complexes6,7). However, the corresponding anionic polymerizations have been studied only scarcely. Fukuchi et al.8) reported the anionic coordination polymerization of epoxides by a new catalyst system consisting of titanium tetraisopropoxide and photochemically generated phenol. The more powerful monomer ethyl cyanoacrylate (ECA) was polymerized by isocyanate ions generated by photoinduced ligand exchange reactions. In another study Kutal and coworkers9) reported the use of $Pt(acac)_2$ complex in the photoinitiated anionic polymerization of ECA. Initiating species were claimed to be free acetyl acetonate anions produced by the photoexcitation of the complex. Quite recently, we have reported10) on the polymerization of ECA initiated by pyridine formed by anthracene-sensitized photodecomposition of N-alkoxy pyridinium ions (Eq. (1) and (2)).



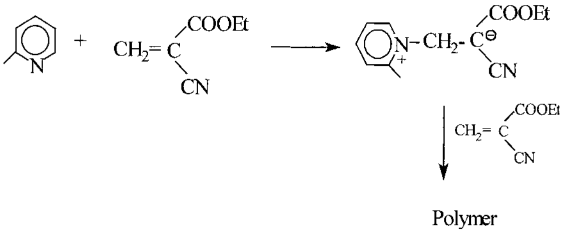
(A)

(1)



(2)

Initiation of polymerization is identical to that described for deliberately added amines11) and involves addition of the photochemically liberated pyridine to the monomer, thus forming zwitterionic species10) (Eq. 3).



(3)

As a part of our continuous interest in photoinitiating systems, we report here the photoinitiated polymerization of ECA with phosphonium salts. As it will be shown

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below, both zwitterionic and free radical mechanisms, although at different rates, are operative in the polymerization.

Experimental

Materials

Benzyl triphenylphosponium hexafluoroantimonate (BP^+) was synthesized according to a procedure described elsewhere[12)], melting point and spectral characteristics were in good agreement with the literature values. Methyl methacrylate (MMA) and dichloromethane (CH_2Cl_2) were purified by conventional drying and distillation procedures. 9-(Chloromethyl)anthracene, triphenylphosphine, ethyl cyanoacrylate (ECA), isopropanol, hydroquinone, $NaSbF_6$, methanesulfonic acid and methanol were used as received.

Synthesis of (anthracen-9-ylmethyl)triphenylphosphonium hexafluoroantimonate (MAP^+)

A mixture of 9-chloromethylanthracene (12 mmol) and triphenylphosphine (10 mmol) was heated at 80 °C and the product was extracted with ether-water. The obtained phosphonium salt in water was treated with $NaSbF_6$ (10 mmol) to yield the corresponding phosphonium salt exchanged with SbF_6. The crude product was recrystallized from isopropanol; yield 75%, m.p. 256 °C.

^1H NMR ($CDCl_3$, δ/ppm): 8–6.2 (m, 24H; 3 Ph and anthracenyl protons), 5.4 (d, 2H; CH_2).

Photopolymerization

Appropriate solutions of monomer, phosphonium salt, hydroquinone and methanesulfonic acid (10 ppm) were degassed with nitrogen and then irradiated in a photoreactor equipped with 15 Philips lamps at room temperature. Light intensity was measured by an Aberchrome actinometer and found to be $6.12 \cdot 10^{-5}$ Einstein · s^{-1}. At the end of a given reaction time, polymers were obtained from the reaction mixture by precipitation into methanol and drying in vacuo.

Analysis

^1H NMR spectra were recorded on a Bruker AM 200 type instrument in $CDCl_3$ with tetramethylsilane as an internal standard. UV/Vis spectra were taken on a Perkin Elmer Lambda 2 spectrometer. Fluorescence spectra were taken on a Perkin Elmer Model LS-50 spectro fluorimeter.

Results and discussion

Phosphonium salts used in this study were prepared by the reaction of triphenylphosphine with chloromethylated aryls followed by counter anion exchange with $NaSbF_6$ according to the known procedure[12)]. Chloromethylated aryl moieties were selected so as to yield the corresponding salts absorbing at different wavelengths (Tab. 1).

Tab. 1. Absorption characteristics of phosphonium salts in CH_2Cl_2.

Salt	λ_{max} (nm)	ε (L mol^{-1} cm^{-1})
BP^+	261	12440
MAP^+	359	6561
MAP^+	378	9555
MAP^+	398	8300

Tab. 2. Photopolymerization[a)] of ECA in the presence of phosphonium salts.

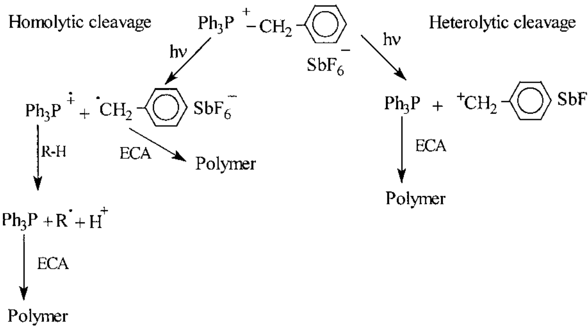
Run	Salt	Hydroquinone	Rp (mol L^{-1} s^{-1})
1	BP^+	–	0.373
2	BP^+	+	0.298
3	MAP^+	–	0.945
4	MAP^+	+	0.472

[a)] Solvent CH_2Cl_2, [ECA] 4.41 mol L^{-1}, [salt] = $1 \cdot 10^{-2}$ mol L^{-1}, [hydroquinone] = $2 \cdot 10^{-2}$, time 1 h.

The photoinitiated polymerization of ECA with phosphonium salts, namely benzyltriphenylphosphonium hexafluoroantimonate (BP^+) and (anthracen-9-ylmethyl)-triphenylphosphonium hexafluoroantimonate (MAP^+), was carried out in CH_2Cl_2 and the conversion of ECA was 24% for BP^+ and 77% for MAP^+ suggesting their photoinitiator activity (Tab. 2).

The relatively low activity of BP^+ seemed to come from weak absorptions beyond 300 nm. Apparently, the phosphonium ion possessing a polyaromatic ring, MAP^+, shows fairly strong absorptions above 300 nm and better initiator activity.

Upon irradiation, phosphonium ions undergo both homolytic[13, 14)] and heterolytic[15)] cleavage of the carbon-phosphorus bond. The heterolytic pathway generates a benzyl cation and triphenylphosphine, whilst a benzyl radical and triphenylphosphonium radical cation are formed on homolytic cleavage (Eq. 4).



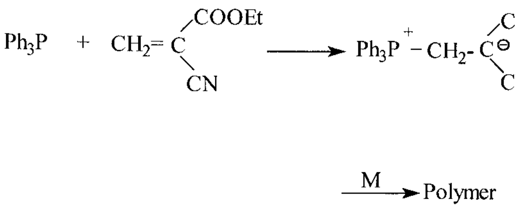
(4)

An electron transfer mechanism as illustrated in Eq. (5) and (6) for tetraphenylphosphonium chloride should also be considered for radical and triphenylphosphine (Ph_3P) generation.

$$Ph_4P^+Cl^- \xrightarrow{h\nu} Ph_4P^{\bullet} + Cl^{\bullet} \quad (5)$$

$$Ph_4P^{\bullet} \longrightarrow Ph_3P + Ph^{\bullet} \quad (6)$$

The weak base, Ph_3P, formed by the reactions shown in Eq. (5) and (6), is supposed to be the primary initiating species[11)] in the photopolymerization of ECA (Eq. 7).



$$Ph_3P + CH_2{=}C(COOEt)(CN) \longrightarrow Ph_3\overset{+}{P}-CH_2-\overset{\ominus}{C}(COOEt)(CN) \xrightarrow{M} \text{Polymer} \quad (7)$$

In addition to the zwitterionic polymerization, radicalic intermediates, formed by homolytic cleavage of the phosphonium ion, may initiate the free radical polymerization of ECA. The contribution of a free radical process in the polymerization is 20% and 50% for BP^+ and MAP^+, respectively, as was determined from the differences of the polymerization rates (Rp) in the presence and absence of hydroquinone as a radical scavenger (Tab. 2).

The structure of the polymer obtained in the polymerization of ECA initiated by MAP^+ in the presence of hydroquinone was examined to consider the mechanism of the polymerization. The polymer insoluble in methanol showed no fluorescence by UV irradiation, suggesting that the anthracenyl group was not incorporated into the polymer chain. Interestingly, the same polymerization in the absence of the radical scavenger yielded a polymer with some fluorescence activity indicating the incorporation of the anthracen-9-ylmethyl group in the polymer (Fig. 1). Therefore, the polymerization is considered to proceed via both radical and zwitterionic mechanisms.

More convincing evidence of the nature of the polymerization mechanism was obtained from the experiments on the polymerization of MMA. Irradiation of the monomer solution in CH_2Cl_2 ([MMA] = 4.68 mol L^{-1}) containing 10^{-2} mol L^{-1} BP^+ gave a polymer with 1.3% conversion after 1 h. Irradiation in the presence of $2 \cdot 10^{-2}$ mol L^{-1} hydroquinone failed to produce any polymer under the same experimental conditions. These results reveal that the less electrophilic monomer MMA is not polymerizable by the weak base Ph_3P, and only the radicalic species reacts with MMA. It should be pointed out that previous studies on the photoinitiated polymerization of MMA with various phosphonium salts suggested only a free radical mechanism[16)].

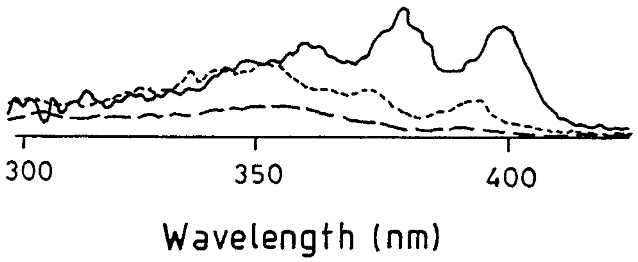
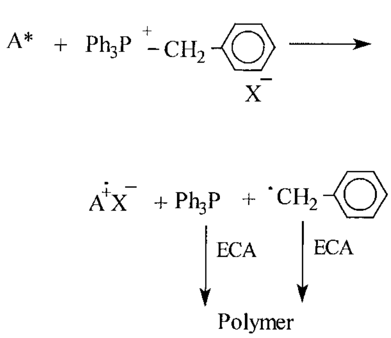


Fig. 1. Fluorescence spectra of 10^{-4} mol L^{-1} toluene solutions of (——) MAP, (- - -) PECA (run 3), (– –) PECA (run 4).

The photoinitiated polymerization of ECA with BP^+ can be sensitized by polyaromatic sensitizers such as anthracene. This way the wavelength sensitivity of BP^+ is extended to longer wavelengths and the photoinitiation activity is increased. A plausible mechanism involves electron transfer from the photoexcited sensitizer to the phosphonium salt (Eq. (8) and (9)) as described for alkoxypyridinium salts[17, 18)].

$$A \xrightarrow{h\nu} A^* \quad (8)$$



(9)

Tab. 3. Anthracene sensitized photopolymerization[a)] of ECA in the presence of BP^+.

Run	BP^+ mol L^{-1}	Anthracene (mol L^{-1})	Hydroquinone (mol L^{-1})	Rp (mol L^{-1} s^{-1})
5	$1 \cdot 10^{-2}$	$2.8 \cdot 10^{-2}$	$2 \cdot 10^{-2}$	0.238
6	$1 \cdot 10^{-2}$	$2.8 \cdot 10^{-2}$	–	0.388

[a)] Solvent CH_2Cl_2, [ECA] = 4.41 mol L^{-1}, time1 h.

In this case, both radical and zwitterionic mechanisms are operative, i.e., the polymer is formed in the absence and presence of a radical scavenger (Tab. 3).

In conclusion, these preliminary studies indicate that phosphonium salts are capable of photoinitiating both free radical and zwitterionic polymerization when the monomer is ECA, but just free radical polymerization when the less electrophilic monomer MMA is utilized. It is possible to carry out the polymerization by direct as well as sensitized irradiation.

We thank the Turkish State Planning Institute (DPT) for financial support.

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