Silver Olefin Complexes: Highly Efficient Initiators for the Electron Beam Curing of Epoxy Resins

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In recent years, remarkable progress has been made in the nonthermal curing of epoxy resins by electron beam (EB) induced cationic polymerization,[1−3] and several studies have been carried out to investigate the curing mechanism and the influence of various parameters on processing and material properties.[4−13] Compared to thermal curing, EB processing offers, especially in the manufacture of high-performance composites, several advantages such as improved resin stabilities at ambient temperature, reduced tooling and processing costs, reduced curing times and fast throughput, curing at ambient temperature, low-energy consumption, and avoiding of hazardous cross-linking agents or volatiles emissions.[14−17] Since the pioneering work of Crivello and co-workers,[18] highly efficient cationic photoinitiators based on onium salts such as diaryliodonium and triarylsulfonium salts became established for the UV curing of a series of cationically polymerizable monomers including epoxides.[19,20] In the meantime it was demonstrated that these initiators show also high activities in the EB curing of epoxy resins, and materials with excellent properties could be obtained using diaryliodonium and triarylsulfonium salts with bulky and weakly nucleophilic anions such as hexafluoroantimonate and fluorinated tetraphenyl borates.[21−23] Metal complexes such as cationic cyclopentadienyl iron(II) arene complexes[24] have also been tested as initiators but revealed significantly lower activities compared to their diaryliodonium and triarylsulfonium analogues.[25]

Here we wish to introduce silver olefin complexes as a new class of highly efficient initiators for the EB curing of epoxy resins. The complexes can be easily prepared by reaction of $AgSbF_6$ with the respective olefins in toluene or THF as solvent. The products precipitate from the reaction mixtures and can be isolated by filtration. A wide variety of monoolefins such as *trans*-2-octene, cyclohexene, cyclooctene, cyclododecene, 5-norbornene-2-carboxylic acid, or 1R-(−)-nopol can be used as well as diolefins such as 1,5-hexadiene, 1,7-octadiene, 1,9-decadiene, sorbic acid ethyl ester, 1,3-cyclohexadiene, 1,3- and 1,5-cyclooctadiene, 2,5-norbornadiene, or dicyclopentadiene and olefins with three or more functional groups, e.g., cycloheptatriene, *trans,trans,cis*-1,5,9-cyclododecatriene, *trans,trans,trans*-1,5,9-cyclododecatriene, cyclooctatetraene, or squalene. The coordination sphere of the silver cation is flexible, and the number of double bonds coordinated to the metal center can be two, e.g. in $[Ag(cyclohexene)_2]SbF_6$, three, e.g. in $\{[Ag(1,7\text{-octadiene})_{1.5}]SbF_6\}_n$, or four, e.g. in $[Ag(1,5\text{-cyclooctadiene})_2]SbF_6$. Olefins with more than one double bond can yield coordination polymers. Thus, X-ray diffraction analysis of the 1,7-octadiene complex reveals a one-dimensional polymeric chain structure (Figure 1) with metal centers alternately linked by one and two 1,7-octadiene moieties.

Most of the silver complexes show good resin solubilities. The epoxy novolacs DEN 431 and DEN 438 as well as mixtures of these resins were chosen as test systems to evaluate the activities of the complexes. Low initiator concentrations, typically 1 or 2%, were used, and 4 mm thick samples were irradiated using an industrial Rhodotron accelerator with a maximum beam output power of 190 kW operating at 10 MeV. The total irradiation dose was 132 kGy subdivided in four irradiation passes of 33 kGy per pass with a dose rate of ~5 kGy s^{-1}. The elapsed time between passes was 20 min in each case. Temperature rises up to peak temperatures above 200 °C were observed using temperature measuring tapes attached to the samples. Characterization of the materials was carried out directly after irradiation without any postcure step and fundamental material parameters such as glass transition temperatures (T_g), Young's moduli, and cross-linking degrees were determined to elucidate the efficiency of the initiators (Table 1). Data obtained with commercially available 4-isopropyl-4′-methyldiphenyliodonium tetrakis(pentafluorophenyl)borate (Rhodorsil 2074), a highly efficient iodonium salt initiator, are also given for comparison. High cross-linking degrees ranging from 91 to 99% were observed, even at low initiator loadings of 1 or 2%. Using the iodonium salt initiator high values around 97% could be obtained, which could also be attained employing the silver 1,7-octadiene complex $\{[Ag(1,7\text{-octadiene})_{1.5}]SbF_6\}_n$. The values correspond to fractional epoxy conversion and were determined by FT-IR spectroscopy before thermomechanical testing. Young's moduli ranging from 3000 to 4000 MPa were measured, and comparing Rhodorsil 2074 with the silver complex $\{[Ag(1,7\text{-octadiene})_{1.5}]SbF_6\}_n$, almost the same values around 3600 MPa were reached using an initiator content of 1%. Glass transition temperatures from 177 up to 233 °C were observed depending on the resin as well as the initiator type and concentration. Because of its higher functionality, epoxy novolac DEN 438 provides materials with considerably higher glass transition temperatures than DEN 431. Using mixtures of both resins, glass transition temperatures increase with increasing content of DEN 438. Samples cured with 1% of Rhodorsil show higher T_g's than comparable mixtures with silver complexes. However, high T_g's above 200 °C could also be achieved by employing higher concentrations of silver complexes and increasing the amount of DEN 438 in the resin mixtures. Thus, the high T_g of 233 °C obtained by polymerizing DEN 438 with 1% of iodonium initiator could also be reached by using 2% of $[Ag(cycloheptatriene)_2]SbF_6$ as initiator.

The epoxy polymerization is initiated by Lewis acidic and oxophilic Ag^+ species generated by EB irradiation (Scheme 1). Highly reactive metal species emerge after olefin dissociation, capable of epoxy ring opening and starting cationic polymerization. Since nucleophilic species interfere with a cationic

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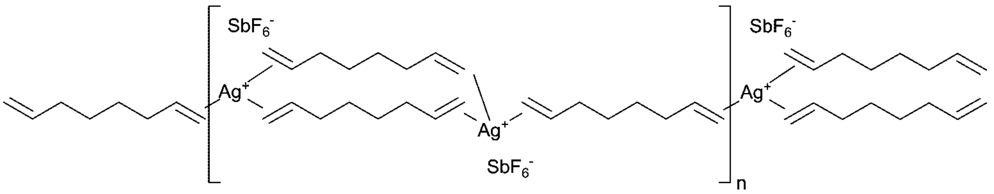


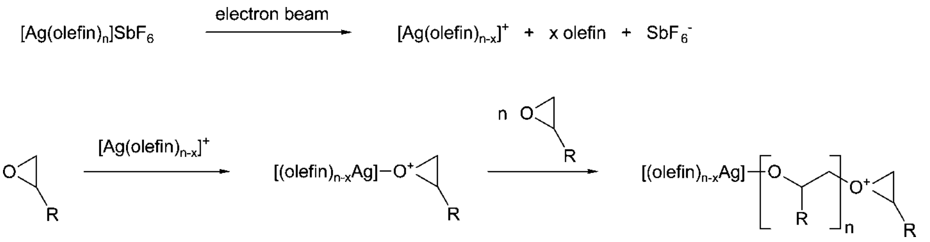
Figure 1. One-dimensional polymeric chain structure of $\{[Ag(1,7\text{-octadiene})_{1.5}]SbF_6\}_n$.

Table 1. EB Curing of Epoxy Novolacs Using Silver Olefin Complexes as Initiators[a]

initiator	resin composition (wt %) initiator	DEN 431	DEN 438	T_g (tan δ)[b] (°C)	Young's modulus[c] (MPa)	cross-linking degree[d] (%)
$[Ag(cycloheptatriene)_2]SbF_6$	1.0	99.0		182	3400	93.6
	1.0	69.3	29.7	201	3400	93.2
	2.0	98.0		177	3500	95.5
	2.0		98.0	233	3000	96.3
$[Ag(cyclohexene)_2]SbF_6$	1.0	99.0		185	3500	91.1
	2.0	98.0		190	3100	91.4
	2.0		98.0	201	3500	92.4
$[Ag(1,5\text{-cyclooctadiene})_2]SbF_6$	2.0	98.0		187	3400	96.8
	3.0	97.0		183	3500	96.4
$\{[Ag(1,7\text{-octadiene})_{1.5}]SbF_6\}_n$	1.0	99.0		184	3600	99.2
	2.0	98.0		190	3100	95.1
	1.0	89.1	9.9	185	3000	91.8
	2.0	88.2	9.8	188	3800	93.5
	1.0	69.3	29.7	190	3600	90.8
	2.0	68.6	29.4	199	3500	95.1
	1.0	49.5	49.5	203	3900	92.4
	2.0	49.0	49.0	201	3100	96.8
	1.0		99.0	204	3600	99.4
	2.0		98.0	217	3300	96.9
Rhodorsil 2074	1.0	99.0		205	3500	96.4
	1.0	69.3	29.7	211	3600	97.0
	1.0		99.0	233	3500	98.2

[a] Electron beam energy: 10 MeV; dose: 4 × 33 kGy. [b] Determined by DMA in the torsion mode with a heating rate of 3 °C min^{-1} between 25 and 300 °C at a frequency of 1 Hz and 0.1% imposed strain. [c] Determination by means of compact tension specimens (CT) in the opening mode test according to ISO 13586. [d] Fractional epoxy conversion determined by FT-IR spectroscopy before thermomechanical testing.

Scheme 1. Ag^+-Initiated Cationic Polymerization of Epoxides upon EB Irradiation



mechanism and lower the initiator efficiency, the nucleophilicity of the involved species has to be kept to a minimum. Thus, corresponding silver complexes with nucleophilic ligands such as nitriles show much lower initiator activities, whereas weakly nucleophilic chelating ligands, e.g. crown ethers, can also be used. Besides the ligands, the anions play a key role, and activities of the silver initiators are inversely related to the nucleophilicity of the anion. As described for the onium salt initiators, efficiency increases in the order $BF_4^- < PF_6^- < AsF_6^- < SbF_6^- \approx B(C_6F_5)_4^-$.[26] Epoxy resins containing the silver complex $[Ag(1,5\text{-cyclooctadiene})_2]BF_4$ could be cured only partially even with high initiator contents of 5%, whereas the corresponding complex with the SbF_6^- anion revealed high activity (Table 1). Preliminary results obtained by use of the 1,7-octadiene complex of $AgB(C_6F_5)_4$ indicated a high initiator efficiency comparable to $\{[Ag(1,7\text{-octadiene})_{1.5}]SbF_6\}_n$.

The corresponding olefin complexes with other metals, e.g. copper, can be obtained by reaction of the respective metal halogenide with $AgSbF_6$, removal of AgCl, and reaction of the metal hexafluoroantimonate with the olefin. The copper complex $[Cu(1,5\text{-cyclooctadiene})_2]SbF_6$ showed similar activity compared to its silver analogue.

Table 2. Pot Life of DEN 431 Containing $\{[Ag(1,7\text{-octadiene})_{1.5}]SbF_6\}_n$

initiator content (%)	storage temperature	daylight	pot life[a]
1	ambient temperature	no	>360 days
1	ambient temperature	yes	10 days
1	100 °C	yes	4.8 h
2	ambient temperature	no	360 days
10	80 °C	yes	4.6 h

[a] Resin viscosity stays unchanged during the given period.

Resins containing the silver initiators exhibit good storage stabilities (Table 2). The systems are light sensitive, and exposure to light reduces their pot lives considerably. Provided that the system is stored in the dark, DEN 431 containing 1% of $\{[Ag(1,7\text{-octadiene})_{1.5}]SbF_6\}_n$ is still unaltered after 1 year at ambient temperature, and the initiator activity is unchanged. Pot life drops to a few days if the resin is exposed to daylight.

The system can be kept at 100 °C for a few hours, even in the presence of daylight, and almost the same behavior is observed using a high initiator loading of 10% and a temperature of 80 °C. Thus, processability of the resin systems during some hours at elevated temperatures is guaranteed.

In summary, we demonstrated that silver olefin complexes of the type $[\mathrm{Ag(olefin)}_n]\mathrm{SbF}_6$ are highly efficient initiators for the EB curing of epoxy resins. The complexes can be prepared conveniently by reaction of AgSbF_6 with a series of olefins, and they can compete with the most efficient state-of-the-art initiators based on iodonium and sulfonium salts. Processing parameters of the resin systems such as reactivity, viscosity, thermal latency, or compatibility with other additives as well as material parameters such as glass transition temperatures, toughness, or thermal and mechanical resistance can be controlled and adapted to the respective requirements by choice of the appropriate olefin ligand. The resin systems are further optimized at present and successfully employed as matrix resins for the manufacture of high-performance carbon fiber-reinforced composites. The complexes are also tested as initiators for a series of other cationically polymerizable monomers.

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Supporting Information Available: Synthesis and characterization of the initiators and experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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