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Synthesis and Investigation of *m,m'*-Dimethoxybenzyl Esters as Novel Organic Soluble Cationic Photoinitiators

Michael G. Mikhael,[†] Anne Buyle Padias, and H. K. Hall, Jr.*

C. S. Marvel Laboratories, Chemistry Department, The University of Arizona, Tucson, Arizona 85721

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ABSTRACT: The cationic homopolymerizations of *N*-vinylcarbazole, 1-methoxy-1,3-butadiene, isobutyl vinyl ether, *p*-methoxystyrene, and cyclohexene oxide using three *m,m'*-dimethoxybenzyl esters as initiators have been investigated under both photochemical and dark conditions. The comparison between the thermal polymerization and photopolymerization rates revealed that these initiators work mainly via a photocationic initiating mechanism. Only *N*-vinylcarbazole produced high molecular weight polymer; the other monomers produced only low molecular weight polymers (10^2–10^3). The order of the reactivity of these initiators is *m,m'*-dimethoxybenzyl 2,4,6–triisopropylbenzenesulfonate (DMB-TIBS) > *m,m'*-dimethoxybenzyl *m*-nitrobenzenesulfonate (DMB-NBS) > *m,m'*-dimethoxybenzyl tosylate (DMB-T). Changing initiator concentration and reaction temperature affected the polymerization yield but had little influence on the polymer molecular weight. Increasing the monomer nucleophilicity and the stability of the formed counterions enhanced the polymerization rate and raised the product molecular weight. A photochemical initiation mechanism was suggested for these systems.

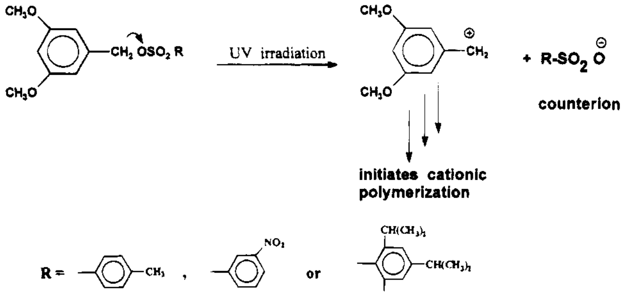
Introduction

Cationic polymerization is one of the major mechanisms of polymerization. It is widely applicable for both vinyl and ring-opening polymerization.[1] Recently, cationic photoinitiation has aroused great interest in both academic and industrial circles.[2] Crivello[3] and Ledwith[4] reported that diaryliodonium or triarylsulfonium salts (e.g., SbF_6^- or PF_6^-) undergo photocleavage and generate strong Brønsted acids which can initiate the cationic polymerization. Still there are some problems facing these onium salts as initiators, namely, poor miscibility in organic medium and incompatibility with nonpolar monomers. In addition, these salts often contain heavy metals which are highly toxic.

In our previous work we have reported that moderately electron-rich olefins, such as *p*-methoxystyrene or vinyl ethers, homopolymerize when they are reacted with electron-poor olefins containing a leaving group.[5–7] Thus these acceptor olefins act as initiators for thermal cationic polymerization and they are purely organic, i.e., not salts.

In this work we report on the synthesis and investigation of a new class of purely organic initiators, but in this case they are photocationic. Zimmerman et al.[8] studied the substituent effects in the photosolvolysis of benzyl acetates. They found that, in the photoreaction, the methoxy group in the meta position was strongly rate enhancing. This is in sharp contrast with the ground state behavior. In the ground state the expected increased π-electron density was found at the ortho and para positions relative to an electron-donating substituent such as methoxy, while in the first excited state selective electron transmission to the ortho and meta positions was noticed. The increased electron density at these sites helps to stabilize the positive charge of the benzyl cation intermediate. These results encouraged us to investigate the potential of benzyl esters substituted in the meta position with electron-donating groups as photocationic organic initiators.

Scheme 1



Results

Initiator Design and Synthesis. Zimmerman[8] investigated the photosolvolysis of *m,m'*-dimethoxybenzyl acetate. However, the acetate is not a suitable counterion in a cationic polymerization. Therefore, we designed esters which would produce stable nonnucleophilic counteranions, such as sulfonates, during the photolysis process. We chose the following *m,m'*-dimethoxybenzyl esters: *m,m'*-dimethoxybenzyl tosylate (DMB-T), *m,m'*-dimethoxybenzyl *m*-nitrobenzenesulfonate (DMB-NBS) and *m,m'*-dimethoxybenzyl 2,4,6-triisopropylbenzenesulfonate (DMB-TIBS). We postulate that these esters will readily undergo photocleavage and produce the *m,m'*-dimethoxybenzyl carbocation which would initiate the cationic polymerization and the tosylate, *m*-nitrobenzenesulfonate, and 2,4,6-triisopropylbenzenesulfonate anions, respectively, as the counterions (Scheme 1).

These sulfonate esters were synthesized in good yields according to the method reported by Kochi and Hammond[9] for the synthesis of monomethoxybenzyl tosylates. As shown in Scheme 2, these new initiators were prepared from the reaction of the sodium salt of *m,m'*-dimethoxybenzyl alcohol with the corresponding sulfonyl chloride derivative. They were purified by recrystallization from ether/petroleum ether 1:1 mixture. They are sensitive toward moisture and light. They turn brown after 48 h at room temperature and in daylight. At −5 °C in the dark and dry atmosphere they are stable for several months.

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* To whom correspondence should be addressed.

[†] Permanent address: Department of Chemistry, Faculty of Science, University of Cairo, Giza, Egypt.

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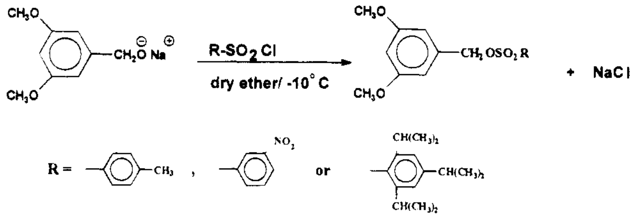
Table 1. Cationic Homopolymerization in CH_2Cl_2 Using DMB-T as Initiator

monomer	monomer conc (mol/L)	init conc (mol %)	temp (°C)	time (h)	photopolymn (% yield)	dark polymn (% yield)	M_w of photopolymer
NVCz	3	0	25	1	3	0	
	3	0.5	25	0.5	88	35	
	0.5	0.2	25	0.5	50		
				1.5	100	trace	1.6×10^5
MBD	bulk	0	25	3	trace	0	
		0.5	25	3	89	7	3550
	4	0.5	25	3	78	0	
IBVE	bulk	0	25	5	0	0	
				24	trace	0	
			50	5	10	trace	1300
		0.5	−10	3	16	0	810
			25	4	40	0	800
				24	80	2	780
			50	4	65	3	760
		1	25	2	40	0	
				4	85	0	790
				6	100		
			45	2	80	3	740
				4	100		
		2	25	3	98	0	750
	4	0.5	25	3	38	0	870
MeOSt	bulk	0	30	5	trace	0	
		0.5	25	3	12	0	4500
		1	25	5	23		
CHO	bulk	0.5	25	3	8	0	8800

Scheme 2



Polymerizations. Five electron-rich monomers were selected to be investigated with our three potential initiators. *N*-Vinylcarbazole (NVCz) is the most electron-rich vinyl monomer in our series. 1-Methoxy-1,3-butadiene (MBD) was taken as an example of an electron-rich conjugated diene. Isobutyl vinyl ether (IBVE), with a low degree of conjugation, was chosen to minimize the interference of the monomer photoabsorption with that of the initiator. *p*-Methoxystyrene (MeOSt) is an example of an aromatic, photoabsorbing, electron-rich monomer. Cyclohexene oxide (CHO) is a representative example for ring-opening polymerization.

All polymerization experiments were run either in bulk or in dichloromethane solutions at the given temperature and reaction time. All experiments started and finished as clear homogeneous solutions, even those in bulk. Blank runs (dark and no initiator) demonstrated the stability of these monomers up to 50 °C for 24 h. Dark reference experiments (no UV light, with initiator) were carried out for comparison.

Table 1 shows the results using the tosylate ester DMB-T as cationic initiator with the five selected monomers. IBVE did not polymerize in the absence of initiator at room temperature; however, 10% yields of polymer (1300 molecular weight) formed at 50 °C after 5 h of UV irradiation. In the presence of 0.5 mol % initiator 40 and 65% yield of polymer was obtained at 25 and 40 °C, respectively. Photopolymerization was even observed at −10 °C. Using 1 mol % initiator resulted in complete reaction (100% conversion) in 6 h at room temperature. In all cases only traces (<3%) of polymer formed in the dark in the presence of DMB-T. MBD showed a higher tendency toward polymerization than IBVE and it produced higher molecular weight polymer (3550). MeOSt and CHO exhibited lower polymerization rates but produced relatively higher molecular weight polymers, 4500 and 8800, respectively. NVCz, the most nucleophilic monomer, showed the highest rate and molecular weight in the presence of DMB-T.

The results obtained using DMB-NBS and DMB-TIBS are summarized in Tables 2 and 3, respectively. Both esters showed higher efficiency as cationic initiators than DMB-T. They only require 3−4 h to achieve almost 100% polymerization of IBVE and MBD at room temperature. No appreciable increase of the molecular weights of the formed polymers was observed. These initiators, in particular the nitrobenzenesulfonate, DMB-NBS, are not convenient for a selective photopolymerization of NVCz because they initiate the polymerization also in the dark. DMB-NBS led to marginal results with MeOSt and is still too unreactive to initiate the ring-opening polymerization of CHO.

For each system an experiment was done in the presence of 2,6-di-*tert*-butyl-4-methylpyridine as a proton trap. No change in polymerization rate could be observed. Also in experiments using IBVE as monomer, tetrahydrothiophene was added to help the stability of the growing carbocation, which might result in increased polymer molecular weight. However, no improvement was observed.

A few exploratory experiments were carried out using divinyl ethers as monomers. DMB-NBS and DMB-TIBS photocationically polymerized either 1,4-bis(divinyloxy)-butane or diethylene glycol divinyl ether at room temperature. These systems produced clear nonsticky coating films after 15−25 min of UV irradiation. The film quality is comparable with that obtained by Sundell et al.[13] when the commonly used iodonium and sulfonium salts were utilized as thermal cationic initiators for these divinyl ethers.

Discussion

Synthesis. We selected the three initiators in this study for two reasons. First, based on Zimmerman's results,[8] the excited *m,m′*-dimethoxybenzyl cation formed

Table 2. Cationic Homopolymerization in CH_2Cl_2 Using DMB-NBS as Initiator

monomer	monomer conc (mol/L)	init conc (mol %)	temp (°C)	time (h)	photopolymn (% yield)	dark polymn (% yield)	M_w of photopolymer
NCz	3	0.5	25	0.1		83	
	0.5	0.2	25	1	100	trace	1.54×10^5
MBD	bulk	0.5	25	3	100	trace	4200
	4	0.5	−3	0.5	27	0	
			−3	5	61	0	4400
			25	3	93	13	
			40	3	98	22	
IBVE	bulk	0.5	25	3	50	0	900
	4	0.5	25	3	56	0	1300
		0.5	50	1	80	4	977
		1	−5	3	61	0	2300
		1	50	1	93	6	1100
MeOSt	3	0.5	25	3	11	0	
				5	14	0	
			50	6	31	5	5100
				24	82	34	
CHO	4	0.5	25	5	7	0	8600

Table 3. Cationic Homopolymerization in CH_2Cl_2 Using DMB-TIBS as Initiator

monomer	monomer conc (mol/L)	init conc (mol %)	temp (°C)	time (h)	photopolymn (% yield)	dark polymn (% yield)	M_w of photopolymer
NVCz	0.5	0.2	25	1	100	10	1.4×10^5
MBD	3	0.5	25	3	90	3	3750
IBVE	4	0.5	25	4	82	0	1100
			40	4	96	trace	950

upon photolysis would be stabilized compared to either the unsubstituted benzyl cation or the ortho- and para-substituted benzyl cations. Second, it is known that sulfonates are relatively stable nonnucleophilic anions. Because the polymerization with the tosylate led to low molecular weight polymers, the nitro derivative (DMB-NBS) was selected to decrease the nucleophilic character of the anion. The electron-withdrawing effect of the *m*-nitro group would increase the stability of the formed counterion (*m*-nitrobenzenesulfonate), especially in the first photoexcited state. DMB-TIBS was selected because its three bulky isopropyl groups are also expected to decrease counterion reactivity.

Polymerization. The results of the UV-irradiated photopolymerizations and dark control polymerizations using DMB-T as a cationic initiator (Table 1) reveal that this initiator behaves as a photocationic initiator. Scheme 1 shows the proposed photocationic initiation mechanism; photolysis of the benzyl esters results in a stabilized benzyl cation and the sulfonate counterion. We propose that this benzyl cation is the initiating species in this system. FT-IR spectral analysis of the produced poly(isobutyl vinyl ether) showed the presence of the benzyl moiety as a chain end group. Except in the case of NVCz, all the formed polymers are of low molecular weight (10^2–10^3). Decreasing initiator concentration and temperature did not markedly affect the polymer molecular weight. This could be due to a strong competition by termination and/or transfer reactions with the propagation process.

Favoring the propagation reaction could be achieved either by increasing monomer nucleophilicity or by decreasing the counteranion reactivity. Changing the monomer led to the following results. MBD showed a higher polymerization rate and molecular weight than IBVE, which might be due to higher monomer electron density and/or higher stability of the growing carbocation. But dark polymerization led to 7% conversion in this system. MeOSt had a lower tendency toward polymerization than IBVE or MBD, but it produced higher molecular weight polymer (4500). The lower yields could be due to photoabsorption interference between monomer and initiator molecules. No dark polymerization was observed in this case. CHO also showed a low rate but relatively higher molecular weight polymer, in this case probably due to low monomer reactivity. On the other hand, NVCz, the most nucleophilic monomer investigated, showed a very fast polymerization reaction and produced film-forming polymers of 10^4 molecular weight. Low monomer and initiator concentration have to be used in this system in order to control and minimize the thermal polymerization.

We also tried to improve the initiator performance by increasing the stability of the produced gegenions. The specific aim was to obtain higher molecular weights for the produced polymers as well as to increase the initiator reactivity. DMB-NBS undergoes photolysis to produce the relatively more stable *m*-nitrobenzenesulfonate anion. As expected, this initiator showed higher efficiency. The introduction of the nitro group markedly increased the polymerization rate and slightly improved the molecular weight of the formed polymers.

DMB-TIBS produces 2,4,6-triisopropylbenzenesulfonate upon photolysis. We postulated that three bulky isopropyl groups would deactivate this anion. Unfortunately, Table 3 shows no major improvement in the polymer molecular weight. Moreover, in spite of the three electron-donating isopropyl groups, this initiator has comparable efficiency to the previous one.

Another attempt to raise the molecular weight was addition of a catalytic amount (1:1 to initiator) of tetrahydrothiophene to stabilize the growing cationic chain. This has been shown to be highly efficient in classical cationic polymerization as described by Matyiaszewski[10] and Webster.[11] But still low molecular weight polymer was produced. Similarly, Percec and co-workers[12] used CF_3SO_3H/Me_2S in CH_2Cl_2 to polymerize vinyl ethers. The produced polymers were of 10–11 degree of polymerization.

When the proton trap 2,6-di-*tert*-butyl-4-methylpyridine was added to the reaction mixture (1:1 to the initiator), no change in polymerization rate was observed. This supports the suggested initiation mechanism (Scheme 1) and removes any probability of initiation by adventitious acids.

Conclusions

We have demonstrated that this novel class of organic initiators can be controlled to act as only photocationic initiators. Any thermal reaction could be avoided by using low concentrations of both monomer and initiator. Increasing monomer nucleophilicity increases the polymerization rate and the polymer molecular weight. Increasing the stability of the counterions produced from initiator photolysis results in a faster polymerization reaction and somewhat higher polymer molecular weight.

Future work in this area will be concerned with modification of the initiator structure to produce more stable counterions upon photocleavage e.g., triflate or diphenyl phosphate.

Experimental Section

Instrumentation. ^{1}H NMR spectra were recorded on a Bruker WM-250 nuclear magnetic resonance spectrometer at 250 MHz. Infrared spectra were recorded on a Perkin-Elmer 982 spectrometer. Melting points were measured with a Thomas-Hoover capillary melting point apparatus and are corrected. SEC data were obtained using THF as eluent, a refractive index detector, and a set of Phenomenex columns calibrated versus polystyrene standards. Elemental analyses were performed by Desert Analytics, Tucson, AZ. A Hanovia medium-pressure mercury lamp (Ace Glass, 7825-34, covers the full spectral range from far-UV to visible) was used as the UV source at 25 cm distance from a double-walled thermostated quartz tube. Ultraviolet spectra were recorded by a Varian DMS 200 UV–visible spectrophotometer.

Solvents and Materials. Methylene chloride (Aldrich) was dried over CaH_2 and distilled before use. Dry diethyl ether and petroleum ether (Aldrich) were used as received. *m,m'*-Dimethoxybenzyl alcohol, *p*-toluenesulfonyl chloride, *m*-nitrobenzenesulfonyl chloride, 2,4,6-triisopropylbenzenesulfonyl chloride, and sodium hydride (Aldrich) were used without further purifications. All the investigated monomers were from Aldrich. MBD, IBVE, MeOSt, and CHO were distilled over CaH_2 just before use. NVCz was recrystallized from methanol and dried under vacuum.

Synthesis of Initiators. The method reported by Hammond[9] was used to synthesize the three investigated initiators. To 0.1 mol of benzyl alcohol, dissolved in 100 mL of anhydrous ether, was added 0.103 mol of sodium hydride. The mixture was stirred and refluxed for 12 h. The suspension of the sodium alcoholate was cooled to −20 °C with a dry ice bath, and a solution of 0.1 mol of the corresponding sulfonyl chloride in 100 mL of anhydrous ether was added dropwise to the suspension. In all operations caution was exercised to exclude moist air from the solutions. The reaction mixture was stirred for 2 h at −10 °C and at room temperature for an additional hour. The suspension was filtered repeatedly with a minimum exposure to air until a clear solution was obtained. When the ethereal solution was cooled to −78 °C, a copious precipitate of fine white needles was obtained. The crystals were quickly filtered and recrystallized several times from dry petroleum ether.

Physical Data of Prepared Initiators. *m,m'*-Dimethoxybenzyl tosylate (DMB-T): white crystals, 52% yield, mp 66–68 °C. λ_{max}(chloroform): 240 nm, $\epsilon = 11000\ L\cdot mol^{-1}\cdot cm^{-1}$. IR (KBr, cm^{-1}): 3105, 3030 (phenyl H); 1595, 1470 (phenyl C=C); 1357, 1175 (SO_2). ^{1}H-NMR ($CDCl_3$) δ 7.81–7.78 (4H, two d); 6.39–6.36 (3H, m); 4.98 (2H, s); 3.84–3.74 (6H, s); 2.44 (3H, s). Anal. Calcd for $C_{16}H_{18}O_5S$: C, 59.58; H, 5.59; S, 9.92. Found: C, 59.43; H, 5.48; S, 9.69.

***m,m'*-Dimethoxybenzyl *m*-nitrobenzenesulfonate (DMB-NBS):** yellowish white crystals, 67% yield, mp 69–71 °C. λ_{max}(chloroform): 243 nm, $\epsilon = 9750\ L\cdot mol^{-1}\cdot cm^{-1}$. IR (KBr, cm^{-1}): 3096, 3022 (phenyl H); 1603, 1478 (phenyl C=C); 1531, 1349 (NO_2); 1360, 1182 (SO_2). ^{1}H-NMR ($CDCl_3$) δ 8.60–8.58 (1H, s); 8.44–8.40 (1H, d); 8.18–8.14 (1H, d); 7.73–7.67 (1H, t); 6.35–6.33 (3H, s, br); 5.15 (2H, s); 3.72 (6H, s). Anal. Calcd for $C_{15}H_{15}NO_7S$: C, 50.95; H, 4.24; N, 3.96; S, 9.06. Found: C, 51.20; H, 4.23; N, 3.94; S, 8.63.

***m,m'*-Dimethoxybenzyl 2,4,6-triisopropylbenzenesulfonate (DMB-TIBS):** gray long needle crystals, 75% yield, mp 79–80 °C. λ_{max}(chloroform): 239 nm, $\epsilon = 7320\ L\cdot mol^{-1}\cdot cm^{-1}$. IR (KBr, cm^{-1}): 3070 (phenyl H); 1600, 1476 (phenyl C=C); 1355, 1175 (SO_2). ^{1}H-NMR ($CDCl_3$) δ 7.18 (2H, s); 6.41–6.40 (3H, s, br); 5.00 (2H, s); 4.17 (2H, m); 3.80–3.74 (6H, s); 2.92 (1H, m); 1.27–1.18 (18H, d, br). Anal. Calcd for $C_{24}H_{34}O_5S$: C, 66.27; H, 7.82; S, 7.36. Found: C, 66.44; H, 7.72; S, 7.25.

Polymerization. Polymerizations were performed on a 0.5 g scale under argon in polymerization tubes equipped with vacuum valves. Photopolymerization experiments were carried out in quartz double-walled thermostated tubes. A Hanovia medium-pressure mercury lamp was used as the UV source (full range) at 25 cm distance from the polymerization tube. Polymer yields were measured, after the given reaction time, by both gravimetric and SEC analyses. SEC was used to determine the molecular weight of the formed polymers.

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