UV-Initiated Reactions of Styrenes with Electrophilic Olefins Having a β-Leaving Group: Partitioning between Free-Radical Copolymerization and Cationic Homopolymerization

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ABSTRACT: Three electrophilic olefins with various β-leaving groups, namely, 1-cyano-1-carbomethoxyvinyl 2-chloride (**I**), 1-cyano-1-carbomethoxyvinyl 2-iodide (**II**), and 2-cyano-2-carbomethoxyvinyl *p*-toluenesulfonate (**III**), reacted under the photochemical conditions with three moderately electron-rich aromatic olefins, styrene, *p*-methylstyrene, and *p*-methoxystyrene, in 1,2-dichloroethane solution at 0 °C. Reaction conditions were adjusted to minimize both the thermal dark polymerization and the photo-self-initiation of the styrenes. The reactivity of these olefins depends on the nature of the leaving group, tosylate > chloride > iodide. The electron-rich character of the styrene monomers also controls the tendency toward cationic homopolymerization: *p*-methoxystyrene > *p*-methylstyrene > styrene. Also the stability of the leaving group anion (tosylate > iodide > chloride) controls the distribution between cationic homopolymerization and free-radical copolymerization. A mechanism was proposed to show the interaction between the excited electron-rich styrene derivative and the electron-poor olefins which leads to the formation of tetramethylene polar 1,4-diradicals. These either initiate the free-radical copolymerization or eject the leaving group anion and create carbocations which initiate the homopolymerization of styrenes.

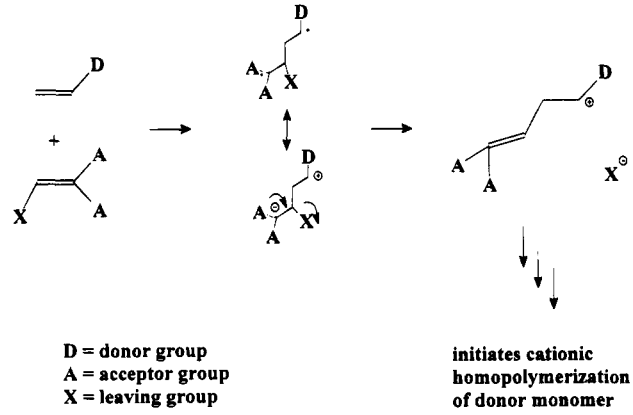
Introduction

In our continuing studies of the spontaneous reactions of electron-rich and electron-poor olefins,[1,2] we have studied the behavior of a particular class of electron-poor olefins, namely, the ones that contain a leaving group at the β-position. 1-Cyano-1-carbomethoxyvinyl-2-chloride (**I**) was first used in initiated free-radical copolymerization with various styrene derivatives and found to copolymerize under the used conditions.[3] When *p*-methoxystyrene was used as the electron-rich comonomer, cationic homopolymerization was observed together with the radical copolymerization (Scheme 1).

Replacing the chloride with better leaving groups, namely, trifluoromethanesulfonate, trifluoroacetate, *p*-toluenesulfonate, or iodide, favored cationic homopolymerization.[4–6] Rasoul[4] reported that 2,2-dicyanovinyl trifluoromethanesulfonate initiated the cationic homopolymerization of *p*-methoxystyrene without copolymerization. Padias[5] synthesized 2,2-dicyanovinyl iodide and 2,2-dicyanovinyl *p*-toluenesulfonate and showed their efficiency to initiate the cationic homopolymerization of *N*-vinylcarbazole and *p*-methoxystyrene. Gong[6] investigated four electrophilic olefins containing β-*p*-toluenesulfonate or β-trifluoroacetate groups as organic initiators for cationic polymerization of both electron-rich vinyl monomers and oxacyclic monomers.

These reactions were explained by invoking the bond-forming initiation theory,[7] in which a bond is formed between the electron-rich and the electron-poor olefins. The resulting tetramethylene will have either predominantly free radical or zwitterionic character. In the case of these olefins with a β-leaving group, the ionic character prevailed. The leaving group is expelled from the tetramethylene intermediate, resulting in a carbocationic species with a rather nonnucleophilic counterion. This proposed mechanism is shown in Scheme 1.

Scheme 1



In order to increase the reactivity range of these olefins, we studied the behavior of the electron-rich and electron-poor olefin mixtures under photochemical conditions. For example, styrene and acrylonitrile do not react spontaneously at room temperature, while under UV irradiation free-radical copolymerization occurs.[8] This is ascribed to excitation of the styrene to a 1,2-triplet diradical, as proposed by Caldwell,[9,10] and formation of a diradical tetramethylene which initiates the copolymerization.

Recently, we also studied the cationic homopolymerization of isobutyl vinyl ether as an electron-rich olefin using 2,2-dicyanovinyl *p*-toluenesulfonate and 2-cyano-2-carbomethoxyvinyl *p*-toluenesufonate as electron-poor initiators.[11] We tried to enhance the initiation of these systems by direct irradiation by UV light. The difference in the reaction rate between the thermal and the photoinduced cationic polymerization was very minimal. These results encouraged us to increase the light-absorbing property of these initiators by introducing the *p*-nitrophenyl group in the β-carbon of these olefins.[11]

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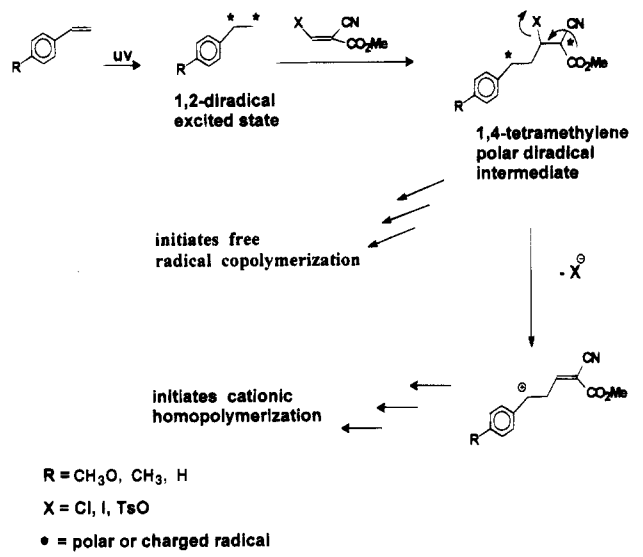
Scheme 2



Again, the obtained improvement was marginal.

Extending our work with the styrene/acrylonitrile system, in this work we will investigate electron-rich styrene derivatives as the donor olefins in the presence of our electrophilic olefins with β-leaving group under UV irradiation. These styrene monomers absorb UV light. We propose that the excited styrene molecules will bond to the electron-poor olefin, just as they did to acrylonitrile, and form tetramethylene intermediate. This may initiate free-radical copolymerization or eject the leaving group anion and form a carbocation which initiates cationic homopolymerization. The cationic polymerization of the styrene would be favored due to the presence of the leaving group in the electrophilic olefins (Scheme 2). The behavior of the monomers will be investigated separately under UV irradiation to rule out self-initiation, as will be the dark reaction of the pairs.

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 983 spectrometer. SEC data were obtained using THF as eluent, an ultraviolet detector, and a set of Phenomenex columns calibrated versus polystyrene standards. 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. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Solvents and Reactants. 1,2-Dichloroethane was dried over CaH_2 and distilled before use. Styrene, *p*-methylstyrene, and *p*-methoxystyrene were received from Aldrich and purified by drying over calcium hydride and distilled under vacuum. The three electron-poor olefins, 1-cyano-1-carbomethoxyvinyl-2-chloride (**I**), 1-cyano-1-carbomethoxyvinyl-2-iodide (**II**), and 2-cyano-2-carbomethoxyvinyl *p*-toluenesulfonate (**III**), were synthesized according to the reported procedures.[2,4]

Polymerization. Photopolymerization was performed on a 0.5 g scale in quartz double-walled tubes under argon atmosphere. In all cases, the temperature was kept constant at 0 °C. After the given reaction time, the reaction mixture was poured into cold methanol in order to precipitate the polymer formed. Reaction yield was determined gravimetrically. Thermal, dark, reference polymerization experiments were carried out in polymerization tubes equipped with vacuum valves.

Table 1. Reactions of Styrene with Three Electrophilic Olefins, in 1,2-Dichloroethane (2 mol/L), at 0 °C for 6 h UV Irradiation

electrophil olefin	concn[a] (mol %)	polym yield[b] (conversn %)	MW SEC	incorp of electrophil olefin (mol %) based on Cl and N
none	0	trace		
I	10	4.0	8000	4
	20	5.8		
	40	6.9	7700	18
	40[c]	0		
II	10	1.5		
	20	2.3		
	40	3.2	8700	trace
	40[c]	0		
III[d]	1	3.0		zero
	2	6.3	9100	
	3	10.6	9700	zero
	3[c]	2.0		

[a] Electrophilic olefin concentration based on styrene. [b] Polymer yield based on styrene feed. [c] Reference experiment done in the dark without UV irradiation. [d] Higher concentration of this olefin causes rapid uncontrolled thermal polymerization.

Results and Discussion

In this paper we investigated the behavior of three electron-poor olefins with a β-leaving group, 1-cyano-1-carbomethoxyvinyl 2-chloride (**I**), 1-cyano-1-carbomethoxyvinyl 2-iodide (**II**), and 2-cyano-2-carbomethoxyvinyl *p*-toluenesulfonate (**III**), as comonomers with styrene, *p*-methylstyrene, and *p*-methoxystyrene under photochemical conditions. 1,2-Dichloroethane was used as the solvent. All reactions were carried out at 0 °C in 2 mol/L solutions. Reaction conditions were adjusted to minimize both the thermal dark polymerization and the photohomopolymerization of styrene monomers. Various electrophilic olefin concentrations were used. Reference experiments were done in the dark and in the absence of the electron-poor olefins. In all the investigated systems, one control experiment was done in the presence of 2,5-dimethyltetrahydrofuran, which is known to be an inhibitor for cationic polymerization.[12] No polymers were produced from the **II** and **III** reactions while a trace of polymer (only weak turbidity) resulted from the **I** system. Experiments run in the presence of a free-radical inhibitor, bis(3-*tert*-butyl-4-hydroxy-5-methylphenyl) sulfide, proceeded unchanged and produced homopolystyrenes. These results reveal that the obtained polymers are mainly produced by a cationic mechanism. A free-radical reaction was observed only in the case of the **I** system. The suggested mechanism in Scheme 2 shows the combination of the excited irradiated styrene molecules with the electrophilic olefins to form tetramethylene 1,4-diradicals, which can initiate the copolymerization of the reacting olefins or eject the leaving group anion and create carbocations that initiate the homopolymerization of the electron-rich olefin.

Styrene. Table 1 shows the results of the reactions of styrene with the three investigated electrophilic comonomers. Under UV irradiation and the abovementioned reaction conditions, only a trace (<0.5%) of homopolystyrene formed in the absence of the electrophilic olefins. This may be attributed to presumption that the excited styrene 1,2-diradical is nucleophilic so it prefers to react with the electrophilic olefin rather than the parent nucleophilic molecule (Scheme 2). In the presence of up to 40 mol % of **I** or **II** , no polymer formed from thermal dark experiments. These results reveal that our system is optimized for photopolymer-

ization initiated by the formed tetramethylene intermediate.

Increasing the amount of **I** from 10 to 40 mol %, under UV irradiation, increased the polystyrene yield from 4 to 7%. Elemental analysis (Cl, N) showed that when 40 mol % **I** was used the produced polymer contains 18% electrophilic olefin. This might be a copolymer or a mixture of copolymer and homopolystyrene with very close molecular weights. Iodo derivative **II** gave lower polymer yields than **I**. Only 3.2% polymer formed when 40 mol % **II** was used. This might be attributed to the lower electrophilicity of **II** relative to that of **I** and to greater steric hindrance at the olefin β-carbon in the case of **II**, which retards the bond formation between the electron-poor and electron-rich olefins. In this case, almost no incorporation of **II** in the produced polymers was observed. The tosylate derivative **III** showed the highest reactivity. Only 3% of this derivative formed 10.6% polystyrene under UV irradiation. This might be due to the stability and high nonnucleophilic character of the tosylate group as a counterion and its electron-withdrawing effect which makes the olefin more electrophilic. When 10 mol % of **III** was used, a fast uncontrollable thermal homopolymerization occurred. All polystyrenes produced from these systems have molecular weight ranges between 7000 and 9700. SEC results showed unimodal spectrograms with 1.3–1.5 polydispersity.

^{1}H NMR spectra of the polymers produced from the **II** and **III** systems showed the typical homopolystyrene spectrum compared to that of polystyrene obtained from bulk photopolymerization of pure styrene. No incorporation of the electron-poor olefins was observed. Also FT-IR analysis did not show any peaks due either to the cyano or to the ester groups of these olefins. On the other hand, polymers produced from the **I** system showed ^{1}H NMR and FT-IR spectra which revealed a comonomer contribution. NMR showed broad band at δ 3.8–4.1. This indicates the presence of the methyl ester group. Also, FT-IR showed a strong absorption band at 1750 cm^{-1}. These spectral data support the elemental analysis results obtained by measuring the Cl and N in the produced polymers. This distribution between the free-radical copolymerization and the cationic homopolymerization (Scheme 2) could be explained on the basis of the stability and nucleophilicity of the leaving group anions. In the case of the chloride derivative **I**, the chloride ion is a poor leaving group and is relatively more nucleophilic toward the propagating carbocations. According to Huisgen's [13] hypothesis, which explains the existence of the tetramethylenes as resonance hybrids of the zwitterions and diradicals forms, this might shift the resonance toward the 1,4-diradicals which will initiate the copolymerization process. In the other cases of **II** and **III**, the iodide and tosylate anions are less nucleophilic; tosylate is almost nonnucleophilic and more stable relative to the chloride ion. This will enhance the ejection of the leaving group anion which creates the carbocation initiators. This cationic mechanism will also be more favored by increasing the electron-rich character of the styrene monomers (see below).

***p*-Methylstyrene.** Table 2 exhibits the results of the reactions of *p*-methylstyrene with our three electrophilic olefins. This monomer showed higher polymer yields than those of styrene, which is ascribed to its more electron-rich character. Again in the **I** and **II** systems (up to 40 mol % electron-poor olefin) no polymers were produced from the thermal dark reactions. Only a trace (<0.5%) of polymer formed, under UV irradiation, in the absence of the electrophilic comonomer. Increasing the amount of **I** from 10 to 40 mol %, under UV irradiation, raised the polymer yield from 4.4 to 18%. When 40 mol % **I** was used, elemental analysis showed only 12% incorporation of this olefin in the formed polymer. That means p-methylstyrene has a higher tendency toward cationic homopolymerization than styrene. This might due to the electron-donating effect of the methyl group, which stabilizes the growing cation (Scheme 2). Again, as in the case of styrene, **II** showed a lower reactivity than **I** and zero incorporation in the obtained polymers. Increasing the concentration of **II** did not affect the polymer yield. The tosylate derivative **III** reacted thermally with *p*-methylstyrene in a very fast uncontrollable manner. Only 1 mol % of this olefin completed the reaction in 2 min without UV irradiation. Therefore this system of **III**/*p*-methylstyrene is not convenient to study the photopolymerization reactions. The molecular weights of the poly(*p*-methylstyrenes) formed from these reactions range between 8000 to 11 000 with ~1.7 polydispersity.

Table 2. Reactions of *p*-Methylstyrene with Three Electrophilic Olefins, in 1,2-Dichloroethane (2 mol/L), at 0 °C for 6 h UV Irradiation

electrophil olefin	concn[a] (mol %)	polym yield[b] (conversn %)	MW SEC	incorp of electrophil olefin (mol %) based on Cl and N
none	0	trace		
I	10	4.4	11000	3
	20	8.9		
	40	17.8	11700	12
	40[c]	0		
II	10	3.6	9800	
	20	3.5		
	40	3.5	10100	trace
	40[c]	0		
III[d]	1	~100[d]	16000	0

[a] Electrophilic olefin concentration based on *p*-methylstyrene. [b] Polymer yield based on *p*-methylstyrene feed. c Reference experiment done in dark without UV irradiation. [d] Thermal polymerization is very fast (1–2 min) and uncontrollable.

Similar to styrene systems, ^{1}H NMR and FT-IR spectral analyses showed zero incorporation of **II** and **III** in the formed poly(*p*-methylstyrenes). In the case of the **I** system, ^{1}H NMR showed a broad band at δ 3.8–3.9 and IR showed a strong peak at 1738 cm^{-1}. This reveals the presence of the electron-poor olefin in the produced copolymers. Again the elemental analysis (Cl and N) results confirm these spectral data.

***p*-Methoxystyrene.** Table 3 shows the data of the reaction of *p*-methoxystyrene, the most electron-rich monomer in our series, with the three investigated electrophilic olefins. As expected, this system shows higher reactivity and greater tendency toward cationic homopolymerization than the other two. Once again only a trace of polymer formed in the absence of the electron-poor comonomer, under UV irradiation. Only 1.5% homopolymer was produced from the thermal dark reactions in presence of 40 mol % **I** and 10 mol % **II**. Raising the amount of **I** from 1 to 40 mol %, under UV irradiation, increased the polymer yield from 4 to 27.5%. At a 40 mol % **I** feed, only 5% of this olefin incorporated into the polymer. Again, this could be attributed to the electron-donating effect of the methoxy group, which increases the stability of the growing carbocation and favors the cationic homopolymerization over the free-

Table 3. Reactions of *p*-Methoxystyrene with Three Electrophilic Olefins, in 1,2-Dichloroethane, at 0 °C for 6 h UV Irradiation

electrophil olefin	concn[a] (mol %)	polym yield[b] (conversn %)	MW SEC	incorp of electrophil olefin (mol %) based on Cl and N
none	0	trace		
I	1	3.9	19300	
	10	7.9	16800	1
	20	11.8	20700	
	40	27.5	20600	5
	40[c]	1.5		
II	1	3.0		
	10	~100	10100	
	10[c]	trace		0
III[d]	1	~100[d]	19900	0

[a] Electrophilic olefin concentration based on *p*-methoxystyrene. [b] Polymer yield based on *p*-methoxystyrene feed. [c] Reference experiment done in dark without UV irradiation. [d] Thermal polymerization is very fast (1-2 min).

-radical copolymerization (Scheme 2). Compound **II** at 10 mol % completed the reaction in the given time without incorporation of the electrophilic olefin in the formed polymer. In this case, still no polymerization was observed in the absence of UV irradiation. It seems that reacting a more electron-rich monomer (*p*-methoxystyrene) with an electrophilic olefin having a leaving group of a moderate nucleophilicity, like iodide, enhances the cationic photopolymerization without increasing the rate of thermal homopolymerization. Also, the higher reactivity of *p*-methoxystyrene toward the cationic homopolymerization, relative to that of styrene, might overcome the steric hindrance described above in the styrene reactions. Olefin **III**, which has a high nonnucleophilic leaving group, showed very fast uncontrollable thermal initiation. Use of 1 mol % **III** produced ~100% homopoly(*p*-methoxystyrene) after only 2 min. The molecular weights of the polymers formed from these reactions range between 16 000 and 20 000. Also in this case, the spectral (NMR, FT-IR) and elemental analyses are in good agreement regarding the polymer structure. Again, the **III**/*p*-methoxystyrene system could not be studied photochemically.

Conclusion

All the obtained data and the reference and control experiments show that these polymerization systems proceed mainly via cationic mechanism with limited competition by free-radical copolymerization in the case of the **I** reactions. These results support the proposed mechanism (Scheme 2). In this mechanism, we suggested that the excited triplet diradicals of the aromatic monomers are formed upon UV irradiation. These excited molecules react with the electrophilic olefins with a β-leaving group to form tetramethylene charged (polar) 1,4-diradicals. These partition between initiating the free-radical copolymerization or eliminating the leaving group anion to create the carbocation initiators, depending on the stability and nucleophilicity of the leaving group anion as well as on the electron-donating character of the electron-rich olefin. Use of moderately nonnucleophilic leaving group such as iodide favors the photocationic polymerization, under the used reaction conditions, without causing fast uncontrollable thermal cationic polymerization, as in the case of the highly nonnucleophilic tosylate group.

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