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Active Centers in the Cationic Polymerization of *p*-Methoxy-α-methylstyrene

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ABSTRACT: Carbocationic species derived from *p*-methoxy-α-methylstyrene (MOS) have been identified by ^{1}H NMR, correlated with UV spectra. The reaction of MOS with trifluoromethanesulfonic acid (HA) in methylene chloride at −63 (NMR) or −72 °C (UV) has given a very stable monomeric cation M^+_1 (A^-, HA) (UV max 367.5 nm; ϵ = 28 500) when a large excess of HA was used. When an excess of monomer is present, dimeric and isomerized trimeric cations are formed, and the UV maximum shifts to 382 nm. The bathochromic shift results from formation of the isomerized species. Carbenium ions are stable at −63 °C, but above −40 °C an indan type dimer is formed that is converted into spirobiindan at room temperature. The equilibrium between the various species stable at −72 °C, which may also involve ethylenic oligomers, is discussed.

Introduction

Cationic polymerization of vinyl monomers is still the most obscure area of chain-growth polymerization processes, even if some aspects have been clarified in recent years. The main difficulty in obtaining reliable kinetic and mechanistic data comes from the high reactivity of carbenium ions that participate not only in chain propagation but also in undesired side reactions (isomerization, transfer, termination).

Detailed studies of initiation reactions have been limited to monomers (such as 1,1-diphenylethylene or 1-substituted indenes) giving stable carbocations (at −30 °C).[1-3] In that case no data on propagation rate constants were available since only the dimerization is thermodynamically allowed and the process is governed by transfer. This is also to date the only example of NMR identification of carbocationic-active species.

Quantitative data on the rate constants of the elementary reactions could also be obtained in systems with stable initiators (e.g., Ph_3C^+, $SbCl_6^-$) and very reactive monomers (vinyl ethers, *p*-methoxystyrene), k_p and k_t being calculated from R_i and R_p in these non-quasi-stationary-state system.[4,5] Lifetimes of active species, derived from kinetics, are of the order of 10–20 s. However, no *direct* verification of the active center's nature or concentration was possible on account of the strong UV absorption of the initiator. For other monomers, such as styrene initiated with protonic acids, the reactivity of the growing species was so high that they appeared as transient carbocations that could only be detected by the stopped-flow technique.[6,7] Carbenium ion concentrations were estimated by assuming the active center extinction coefficient, and their yield based on acid concentration was only a few percent.[6,7] Estimates of rate constants were also given. For more stable carbenium ions derived from α-methylstyrenes, extinction coefficients have been based on data obtained from the corresponding carbinols in superacid media,[8] but the actual growing species might differ from those models of monomeric cations in structure, absorption, and reactivity.

Recently relatively stable carbenium ions were observed in the polymerization of *p*-isopropyl-α-methylstyrene.[9] At low temperature (−58 °C) the cations remained stable for several minutes. We have chosen as a model monomer for these studies *p*-methoxy-α-methylstyrene. The *p*-methoxy group should increase the stability of the carbenium ion even more than the *p*-isopropyl group and it should also decrease the possibility of termination by alkylation of the ortho carbon atoms in the aromatic rings (indanic termination).[10] On the other hand the presence of an α-methyl group should not only increase the stability of the carbenium ion but also yield reversible systems due to the high monomer equilibrium concentration ($[M]_e$) of α-methylstyrenes. Thus, the purpose of this Article is the synthesis and the spectroscopic characterization (NMR, UV) of the real active centers in the cationic polymerization of *p*-methoxy-α-methylstyrene under polymerization conditions, i.e., not in a superacid medium but in the usual solvent dichloromethane.

Experimental Section

Materials. *p*-Methoxy-α-methylstyrene was prepared from *p*-methoxyacetophenone by reaction with methylmagnesium bromide in dry diethyl ether followed by the dehydration of the corresponding alcohol, under reduced pressure, with iodine on a spinning-band column. After distillation (80 °C (2–3 mmHg)), the monomer was dried under vacuum (gas chromatographic purity better than 99.5%) over sodium mirrors and stored at −20 °C.

The corresponding cumyl chloride was prepared by bubbling dry HCl through a CH_2Cl_2 solution of the carbinol. The dried chloride was distilled (42 °C (1 mmHg)) and stored at −20 °C.

Trifluoromethanesulfonic acid (CF_3SO_3H, triflic acid) and SbF_5 were purified several times by distillation in sealed vessels of the commercial products and eventually distributed to capillaries of known diameters equipped with break-seals.

Methylene chlorides (CH_2Cl_2 and CD_2Cl_2) were purified, dried, and stored under vacuum according to procedures described previously.[11]

Procedures. The solution of monomer, triflic acid, and SbF_5 in methylene chloride was prepared under vacuum and distributed to calibrated tubes equipped with break-seals or Teflon stopcocks.

^{1}H NMR Spectroscopy. ^{1}H NMR spectra were obtained with a 250 MHz Brücker spectrometer. The solution of monomer in CD_2Cl_2 was prepared just before the NMR studies.

First, the solution of monomer was transferred to the NMR tube and frozen (after washing the walls of the apparatus). The solution of acid in CD_2Cl_2 was then added and frozen on top of the monomer solution before sealing the tube. The two layers of reactants were melted at −80 °C in a CH_3OH bath and mixed quickly. The tube was then transferred rapidly to the NMR probe kept at −63 °C.

Spectrophotometry. UV–visible studies were carried out under vacuum in CH_2Cl_2 at −72 °C in sealed vessels. The apparatus used was a thermoregulated quartz cell.[12] The cooled monomer increments in CH_2Cl_2 (total volume, 15 mL) in a calibrated tube equipped with a Teflon stopcock were added to the acid solution (30 mL). Spectra were obtained with a CARY 118 spectrophotometer.

Olefinic Oligomers. Oligomerization of *p*-methoxy-α-methylstyrene (44 mM) initiated by CF_3SO_3H (5.7 mM) was carried out at −40 °C under nitrogen in methylene chloride in presence of H_2O traces. After deactivation by sodium methanolate, the oligomers in an ethyl acetate–cyclohexane solution were separated on silica gel.

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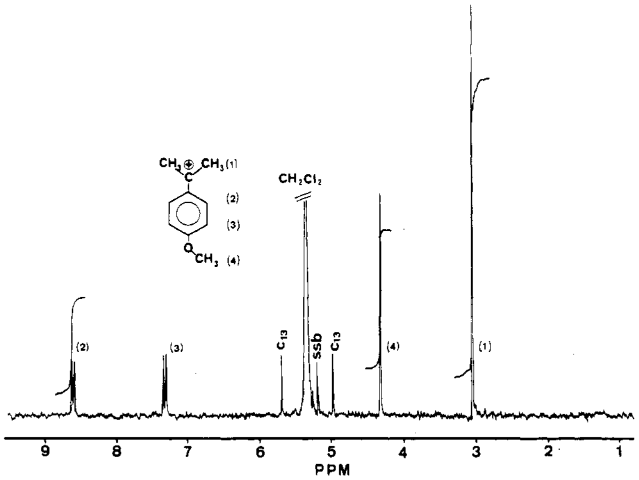


Figure 1. 250-MHz ^{1}H NMR spectrum after reaction of $[M]_0 = 21$ mM and $[HA]_0 = 50$ mM in CD_2Cl_2 at −63 °C.

Results and Discussion

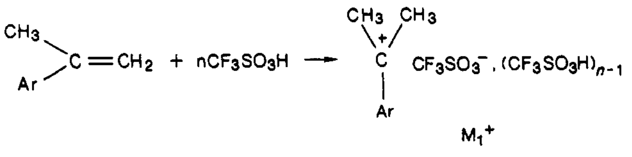
NMR Studies. There are several possibilities for the generation of carbenium ions, the most common being the reaction between olefin and acid or the ionization of an alkyl derivative with a good leaving group. We studied both reactions: protonation of monomers and ionization of the corresponding halides with Lewis acids.

Reaction of Monomer with Triflic Acid. Oligomeric Cations. Protonation of the monomer should lead to the monomeric cation which can, however, react rapidly with the remaining monomer present in the reaction medium to form dimeric, trimeric, and higher oligomeric cations

$$\begin{aligned} HA + M &\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M_1^* \\ M_1^* + M &\overset{k_2}{\rightleftharpoons} M_2^* \\ M_2^* + M &\overset{k_3}{\rightleftharpoons} M_3^* \\ M_n^* + M &\overset{k_n}{\rightleftharpoons} M_{n+1}^* \end{aligned} \quad (1)$$

The relative proportions of the corresponding cations depend on the $[M]_0/[HA]_0$ ratio and on the corresponding equilibrium (or rate) constants. Usually, the ratio of the initiation and propagation rate constants k_1/k_p ($k_p \simeq k_2 \simeq k_3 \simeq k_n$) is low, and only a fraction of the acid is consumed. The product with a degree of polymerization equal to $[M]_0/[HA]_0$ is formed only if $k_1 \gg k_p$ or if the system is fully reversible.

Figure 1 shows the ^{1}H NMR spectrum of a mixture of monomer ($[M]_0 = 2.1 \times 10^{-2}$ mol·L^{-1}) with an excess of triflic acid ($[CF_3SO_3H]_0 = 5 \times 10^{-2}$ mol·L^{-1}) in CD_2Cl_2 at −63 °C. This spectrum corresponds to the monomeric cation (M_1^+)



$$\begin{matrix} CH_3 \\ Ar \end{matrix}\!\!>C{=}CH_2 + nCF_3SO_3H \longrightarrow \overset{CH_3\;\;CH_3}{\underset{Ar}{\overset{+}{C}}}\;CF_3SO_3^-\cdot(CF_3SO_3H)_{n-1} \quad \underset{M_1^+}{} \qquad (2)$$

The methyl groups resonate at 3.04 ppm and the methoxy group at 4.31 ppm. The chemical shifts for the ortho and meta aromatic protons are respectively 8.60 and 7.31 ppm. Similar chemical shifts have been observed in superacid media.[13] At ≃14 ppm is observed the broad signal of the acidic protons, in excess and exchanging with the protonated anion. The consumption of monomer is quantitative. No signals of monomer [cf. Table III) were found in NMR spectra.

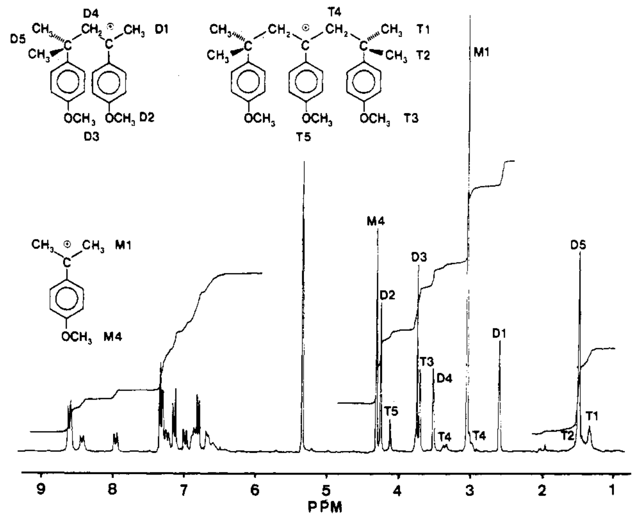


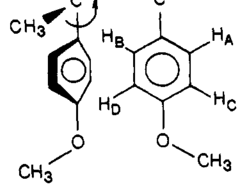
Figure 2. 250-MHz ^{1}H NMR spectrum after reaction of $[M]_0 = 31$ mM and $[HA]_0 = 37$ mM in CD_2Cl_2 at equilibrium ($T = -63$ °C).

This reaction mixture is very stable and when stored at low temperature (−78 °C) does not change during 1 mo. At room temperature spirobiindan is slowly formed (cf. Figure 8). This result indicates high stability of the monomeric cation M_1^+ and also that $k_1 > k_2$.

Figure 2 shows the ^{1}H NMR spectrum of the mixture with a somewhat higher concentration of monomer ($[M]_0 = 3.1 \times 10^{-2}$ mol·L^{-1}, ($[HOSO_2CF_3]_0 = 3.7 \times 10^{-2}$ mol·L^{-1}). Besides the already discussed monomeric cation (M_1^+), two other species are present. This reaction mixture is red contrary to the colorless mixture discussed before (see next section for the UV analysis). One of the species is the cation derived from the linear dimer ("dimeric cation" M_2^+). It has well-defined signals for all the protons (cf. Table I). The methoxy group from the first aromatic ring appears at 4.26 ppm (0.05 ppm upfield from M_1^+) and the second methoxy group at 3.75 ppm. The α-methylene and α-methyl protons resonate at 3.52 and 2.56 ppm, respectively, whereas both terminal methyl groups are at 1.50 ppm.

The aromatic protons from the second ring show a typical AB pattern (ortho, 7.13 ppm; meta, 6.80 ppm; $J_{AB} = 8.7$ Hz). In the first ring, all four aromatic protons have different chemical shifts, revealing a nonequivalence of the ortho and meta protons. The signals at 8.42 and 7.96 ppm are assigned to the ortho protons (more positively charged) and the signals at 7.23 and 6.98 ppm to meta protons. The coupling between the ortho protons ($J_{AB} = 1.5$ Hz) is weaker than between the meta protons ($J_{CD} = 2.5$ Hz). On the other hand both pairs of ortho and meta protons are coupled in a similar way ($J_{AC} = J_{BD} = 9.7$ Hz).

This result indicates that the aromatic nuclei are not in permanent parallel position. One of the possible structures of the dimeric cation M_2^+ is

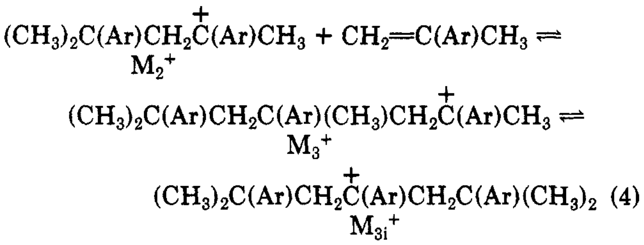


(3)

The bond between the positively charged carbon atom and the aromatic nucleus has a partial character of double bond. The rotation around this bond is slow enough to permit the observation of different signals for each aromatic proton (at −40 °C the rate constant of this process is lower than 200 s^{-1}). On the other hand, the equivalency of the two terminal methyl groups and of the protons in the second ring indicate a relatively rapid rotation around the C–Ar bond.

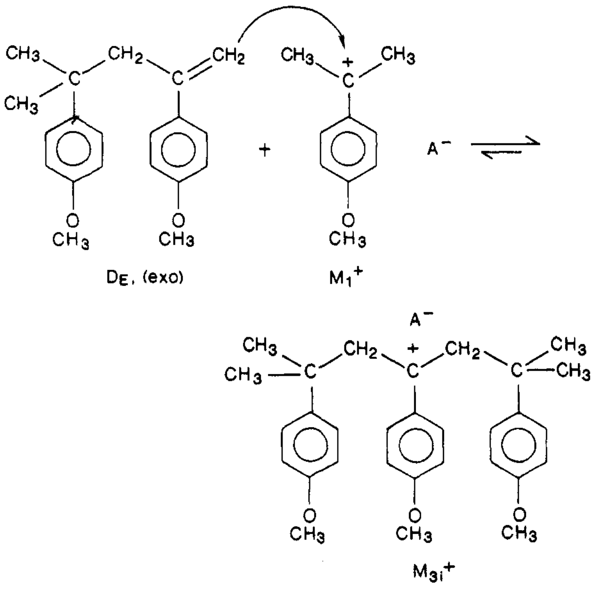
In Figure 2, near the signals of the CH_3O groups of M_1^+ and M_2^+ a third signal is observed that might be ascribed to the CH_3O group of the trimeric cation.

The detailed NMR analysis revealed, however, that this cation does not have the typical linear structure (M_3^+) with the charge located at the chain end but that the charge is located at the central unit. This species could have been formed by an intramolecular 1,3-methyl shift



$$\underset{M_2^+}{(CH_3)_2C(Ar)CH_2\overset{+}{C}(Ar)CH_3} + CH_2{=}C(Ar)CH_3 \rightleftharpoons \underset{M_3^+}{(CH_3)_2C(Ar)CH_2C(Ar)(CH_3)CH_2\overset{+}{C}(Ar)CH_3} \rightleftharpoons \underset{M_{3i}^+}{(CH_3)_2C(Ar)CH_2\overset{+}{C}(Ar)CH_2C(Ar)(CH_3)_2} \quad (4)$$

However, 1,3 rearrangements of carbenium cations usually have a high-energy barrier, contrary to 1,2 shifts, and there is another route to the isomerized trimeric cation M_{3i}^+, involving the exo linear dimer (D_E(exo)) and the monomeric cation



(5)

The reaction with the endo dimer (D_E(endo) eq 6 is less possible due to the steric hindrances.

The cation M_{3i}^+ can hardly react with the monomer due to steric hindrance. Such a reaction should leave a print on the polymer structure leading to branches in polymer chains, but such types of branches have never been observed.

Thus, the isomerized cations may play the role of a dormant species. The first spectra were usually obtained after about 1 min, i.e., after polymerizations had been complete. It might be possible that the isomerized cations are formed after polymerization. However, in the case of *p*-isopropyl-α-methylstyrene, the absorption at 363 nm was observed 20 ms after mixing and then remained stable.[9]

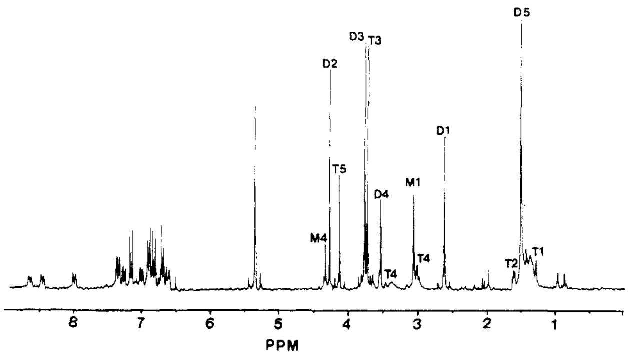


Figure 3. 250-MHz ^1H NMR spectrum after reaction of $[M]_0 = 44$ mM and $[HA]_0 = 38$ mM in CD_2Cl_2 at −40 °C (after 5 min).

The isomerized trimeric cation M_{3i}^+ has much more internal freedom than M_3^+ and should be thermodynamically more stable. The signal of the central methoxy group appears at 4.10 ppm (0.16 ppm upfield from M_2^+, the difference between M_1^+ and M_2^+ being only $\Delta\delta$ 0.05). The side methoxy group absorbs at 3.70 ppm (0.05 ppm upfield from M_2^+). At 3.35 and 3.00 ppm (cf. Figure 4), the methylene protons form a AB system ($J_{AB} = 10$ Hz) (due to the slow rotation in the M_{3i}^+ molecule at low temperature).

One could argue that these signals might be ascribed to the methyl and methylene protons from the nonisomerized trimeric cation M_3^+ but in experiments where only the trimeric cation was present (neither M_1^+ nor M_2^+ were present) the integration showed clearly that each peak corresponded to two protons. Selective irradiation indicates real coupling (no coupling is possible between methyl and methylene protons in the trimeric cation M_3^+). The terminal methyl groups are not equivalent, resembling methylene protons, and resonate at 1.49 and 1.32 ppm.

The aromatic protons from the side rings absorb at 6.86 (ortho) an 6.65 ppm (meta) with a coupling constant $J_{AB} = 8.6$ Hz. The aromatic protons from the central charged ring absorb at 7.23 and 6.60 ppm at a much higher field than similar protons in M_1^+ and M_2^+. This again confirms the isomerized structure of the trimeric cation: the chemical shift at higher field is due to the shielding by two neighboring aromatic nuclei.

In experiment 4 (Figure 3) at a higher temperature (−40 °C) the broadening of the signals of methylene groups and methyl groups is observed. At still higher temperature when the rotation rate increases these signals coalesce ($k = 3 \times 10^2$ s^{-1} at −20 °C).

As the temperature changes, reversible changes of the proportions of the species may be observed. This indicates that the isomerized trimeric cation M_{3i}^+ is in dynamic equilibrium with all the other species.

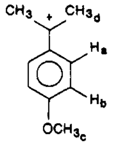
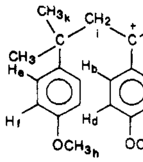
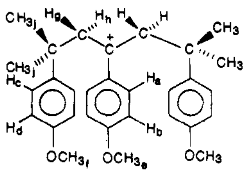
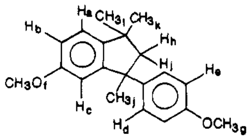
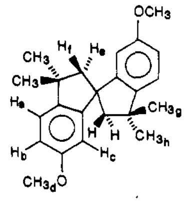
Other experiments were carried out with ratios $\rho = [M]_0/[HA]_0$ higher than 0.5 and the results are reported in Table II.

1. For ratios $0.5 < [M]_0/[HA]_0 < 1.5$ the three species M_1^+, M_2^+, and M_{3i}^+ are observed.
2. For $1.5 < [M]_0/[HA]_0 < 2$ M_2^+ and M_{3i}^+ are found but the active centers have predominantly the structure M_{3i}^+ (Figure 4).
3. For a ratio above 2 only M_{3i}^+ is present.

The proportion of the various oligomeric cations depends on $[M]_0/[HA]_0$ (Figure 5) and confirms the equilibria between the different species (eq 9) with $k_1 \gg k_2 > k_3$.

On the other hand, when the concentration $[HA]_0$ is large enough to be measured by NMR ($>10^{-2}$ mol·L^{-1}), we have always observed the resonance of an acidic proton at lower field (11.0–17.2 ppm).

Table I
Chemical Shifts[a] and Coupling Constants of the Carbocation Species and Indanic Dimers

compd	structure	chem shift	coupling const, Hz
M_1^+		8.60 (H_a), 7.31 (H_b) 4.31 (H_c), 3.04 (H_d)	J_{AB} = 9.2
M_2^+		8.42 (H_a), 7.96 (H_b) 7.23 (H_c), 6.98 (H_d) 7.13 (H_e), 6.80 (H_f) 4.26 (H_g), 3.75 (H_h) 3.52 (H_i), 2.56 (H_j) 1.50 (H_k)	J_{AB} = 1.5 J_{CD} = 2.5 J_{EF} = 8.7 J_{AC} = 9.7 J_{BD} = 9.7
M_{3i}^+		7.25 (H_a), 6.60 (H_b) 6.86 (H_c), 6.65 (H_d) 4.10 (H_e), 3.70 (H_f) 3.35 (H_g), 3.00 (H_h) 1.49 (H_i), 1.32 (H_j)	J_{CD} = 8.6 J_{GH} = 9
D_I		7.12 (H_a), 6.86 (H_b) 7.08 (H_d), 6.79 (H_e) 6.65 (H_c) 3.83–3.79 (H_f–H_g) 2.32 (H_h), 2.15 (H_i) 1.60 (H_j), 1.26 (H_k), 0.91 (H_l)	J_{AB} = 11 J_{DE} = 8.8 J_{BC} = 2.5 J_{HI} = 13
spirobiindan		7.17 (H_a), 6.92 (H_b) 6.42 (H_c) 3.87 (H_d) 2.41 (H_e), 2.34 (H_f) 1.41 (H_g), 1.35 (H_h) after addition of CH$_3$OH 7.10 (H_a), 6.78 (H_b), 6.32 (H_c) 3.69 (H_d), 2.39 (H_e), 2.24 (H_f) 1.39 (H_g), 1.33 (H_h)	J_{AB} = 8.2 J_{BC} = 2.5 J_{EF} = 13

[a] Using nondeuteriated solvent CH_2Cl_2 as internal reference (δ 5.35).

Table II
Relative Proportion of Oligomeric Cations at Various $[M]_0/[HA]_0$ Ratios

expt	T, °C	$10^2[M]_0$, M·L^{-1}	$10^2[HA]_0$, M·L^{-1}	$[M]_0/[HA]_0$	% M_1^+	% M_2^+	% M_{3i}^+
1	−63	0.4	3.07	0.130 0.124[a]	100		
2	−63	2.1	5.0	0.42	100		
3	−63	3.1	3.7	0.83 0.72[a]	54	38	8
4	−60	4.4	3.8	1.16 1.16[a]	18	45	36
5	−65	0.58	0.43	1.35	5	35	60
6	−65	1.62	0.85	1.90		6	94
7	−60	5.0	0.58	8.6			100

[a] Determined by ^{1}H NMR.

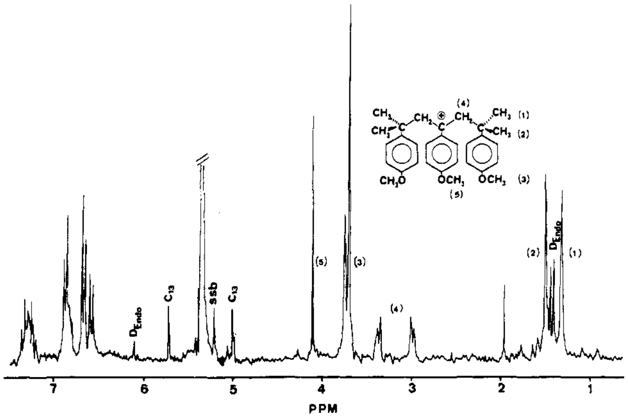


Figure 4. 250-MHz ^{1}H NMR spectrum after reaction of $[M]_0$ = 16.2 mM and $[HA]_0$ = 8.5 mM in CD_2Cl_2 at −65 °C.

From Figure 5 we conclude that for M_1^+, M_2^+, and M_{3i}^+ the counterion has the A^-, HA structure and probably the A^-, nHA structure[3] for M_1^+ at higher concentrations of acid (ρ <0.5).

Unsaturated Oligomers. For ratios $[M]_0/[HA]_0$ higher than 1.5, several new peaks appear in the NMR spectra.

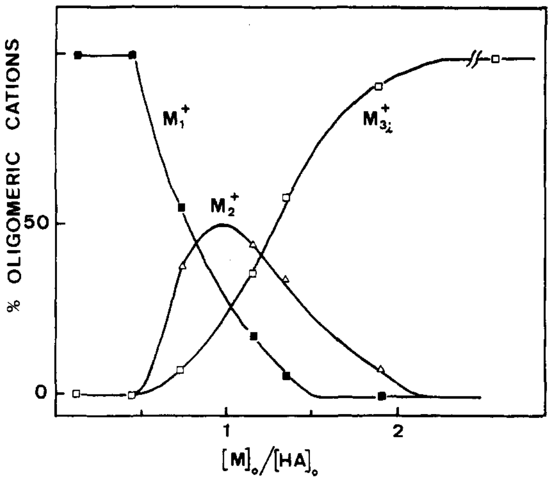
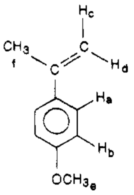
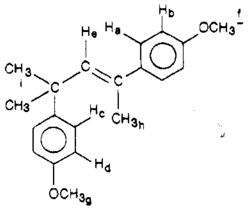
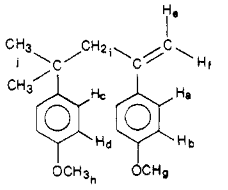


Figure 5. Relative proportions of M_1^+, M_2^+, and M_{3i}^+ at various $[M]_0/[HA]_0$ ratios.

In order to attribute the new signals observed, we have prepared the olefinic dimers (see Experimental Section). The ^{1}H NMR spectra of the two linear dimers show respectively an endo and an exo olefinic bond (see chemical

Table III
Chemical Shifts[a] and Coupling Constants of Ethylenic Oligomers

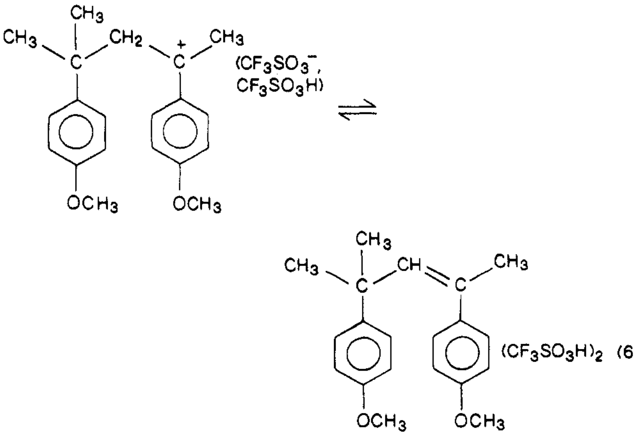
compd	structure	chem shift	coupling const, Hz
M		7.44 (H_a), 6.89 (H_b) 5.31 (H_c) 5.01 (H_d) 3.835 (H_e) 2.155 (H_f)	J_{AB} = 8.9 J_{CD} = 1.5 J_{DF} = 1.5 J_{CF} = 0.8
D_E(endo) (trans)		7.38 (H_a–H_c) 6.86 (H_b) 6.09 (H_e) 3.85 (H_f) 3.845 (H_g) 1.625 (H_h) 1.545 (H_i)	J_{AB} = 8.8 J_{CD} = 8.6 J_{EH} = 1.2
D_E(exo)		7.25 (H_a) 7.22 (H_c) 6.78 (H_b–H_d) 5.15 (H_e) 4.77 (H_f) 3.83–3.82 (H_g–H_h) 2.82 (H_i) 1.262 (H_j)	J_{AB} = 8.8 J_{CD} = 8.8 J_{EF} = 1.8

[a] Using nondeuteriated solvent CH_2Cl_2 as internal reference (δ 5.35) or $CHCl_3$ (δ 7.27).

shifts in Table III). The new absorptions observed in experiments 6 and 7 may be attributed to these two linear dimers.

The chemical shifts observed for the two different methyl groups (1.54 (6 H), 1.62 ppm (3 H)) of the endo dimer may be compared to those of the trans endo dimer obtained in the oligomerization of the α-methylstyrene.[14]

At $[M]_0/[HA]_0 = 1.90$ (experiment 6), the trans endo dimer was found in the first spectrum. With a higher monomer proportion (experiment 7), the exo dimer was formed first. It is possible that the exo dimer is formed rapidly by transfer to monomer (or perhaps by reaction with traces of moisture in the monomer solution) and the trans endo dimer by transfer to counterion, more slowly, in the following way:



(6)

D_E, endo

Initially, in experiment 7, the ratio of endo to exo dimers was 1:4, but it increased with time. At −40 °C, the exo dimer is converted slowly into the thermodynamically more stable trans endo dimer. At this temperature, the isomerized trimeric cations are slowly transformed into the ethylenic trimers

$$(CH_3)_2C(Ar)CH_2\overset{+}{C}(Ar)CH_2C(Ar)(CH_3)_2 \rightarrow (CH_3)_2C(Ar)CH{=}C(Ar)CH_2C(Ar)(CH_3)_2 \quad (7)$$

(CH_3) 0.98, 1.06 ppm; (CH_2) 2.65 ppm

($-CH=$) 5.53 ppm

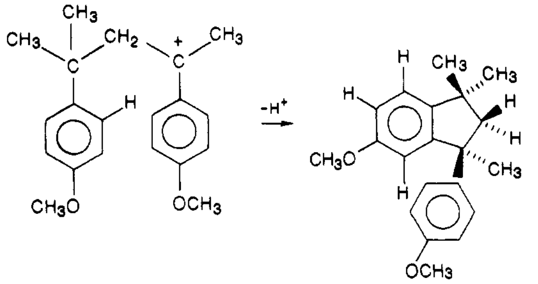
One should notice in Figures 2–4 a tiny singlet at 1.97 ppm. This signal is always absent for a ratio lower than 0.5 (and in the colorless mixture coresponding to Figure 7), whereas it is sometimes present at higher ratios. For example, with an excess of monomer, the intensity of the signal at 1.97 ppm increases, corresponding to more than 20% (experiment 6) or 30 % (experiment 7) of the concentration of the active centres M_{3i}^+.

In the oligomerization of α-methylstyrene, giving the exo dimer and the trans endo dimer, the cis endo dimer has been observed,[14] and for this dimer the methyl group near the double bond absorbs at 1.99 ppm. Thus, in our system, the signal at 1.97 ppm might result from the methyl groups of the cis dimer. The small quantities of this species may hinder finding the signal of the olefinic proton (probably near the CH_2Cl_2 signal) and the signals of the other methyl groups (in the same region as the methyl groups of M_{3i}^+).

Another possibility might be that this signal at 1.97 ppm is due to the methyl group of the monomer complexed with active centers (but no signals of ethylenic protons are observed) or to the methyl group of (p-methoxyphenyl)-dimethylcarbinol present in traces in the monomer solution or formed by reaction of the monomeric cation with H_2O traces.

Final Products. If at very low temperature the oligomeric carbocations are stable, at temperature above −40 °C the indan type cyclic dimer was slowly and irreversibly formed. At still higher temperatures, this reaction is much more rapid.

The spectrum of the reaction mixture (experiment 4) after 3 days at −20 °C is shown in Figure 6. One may observe a strong decrease of the concentration of the trimeric cation M_{3i}^+. The relative proportion of the dimeric cation M_2^+ has also decreased. Besides the predominant monomeric cation M_1^+, the indan type dimer (D_I) is found (see chemical shifts in Table I).



(8)

D_I

Formation of the indan by cyclization of the dimeric cation leads to the decrease of the concentration of the monomer available for the reversible protonation and equilibration to form dimeric and trimeric cations. Thus, the decrease of M leads to the disappearance of M_{3i}^+ (in equilibrium with M_3^+) as well as that of M_2^+. This once again confirms the dynamic equilibration between M_1^+, M_2^+, and M_3^+ (M_{3i}^+)

$$\begin{tikzcd}
HA + M \arrow[r, shift left, "k_1"] \arrow[r, leftarrow, shift right] & M_1^+ + M \arrow[r, shift left, "k_2"] \arrow[r, leftarrow, shift right] & M_2^+ + M \arrow[r, shift left, "k_3"] \arrow[r, leftarrow, shift right] \arrow[d] \arrow[dr, shift left] \arrow[dr, leftarrow, shift right] & M_3^+ \arrow[r, shift left] \arrow[r, leftarrow, shift right] & M_{3i}^+ \arrow[dl, shift left] \arrow[dl, leftarrow, shift right] \\
 & & D_I & D_E + M_1^+ &
\end{tikzcd} \quad (9)$$

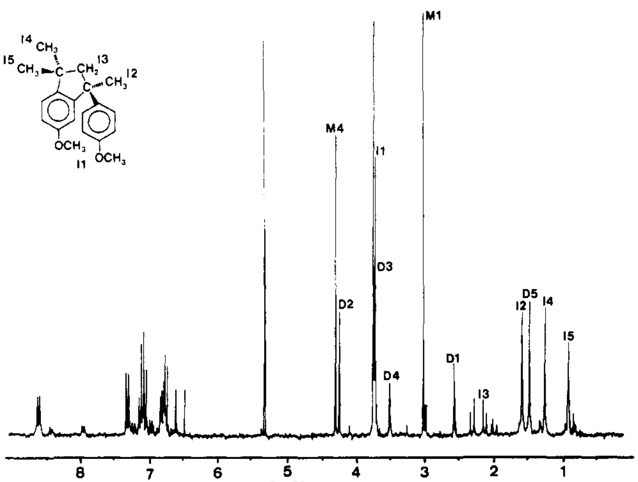


Figure 6. Same as Figure 3 but after 3 days at −20 °C.

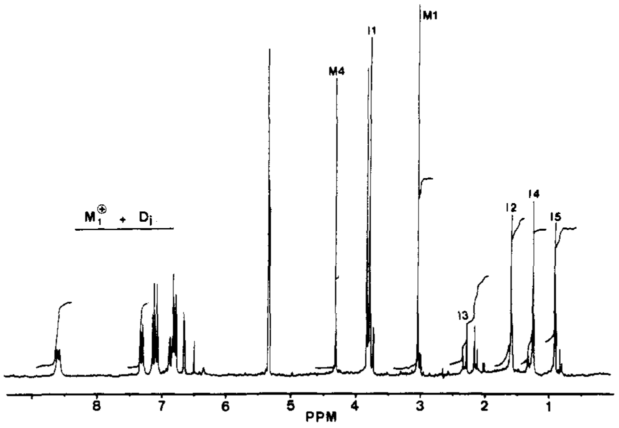


Figure 7. Same as Figures 3 and 6 but after 14 days at −20 °C.

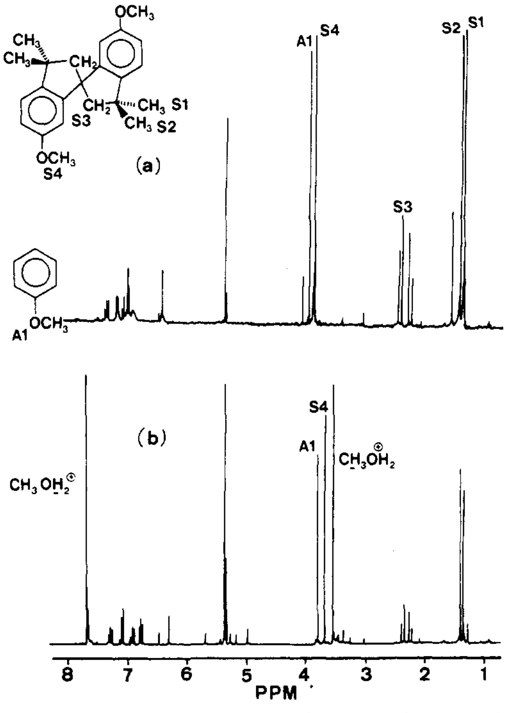
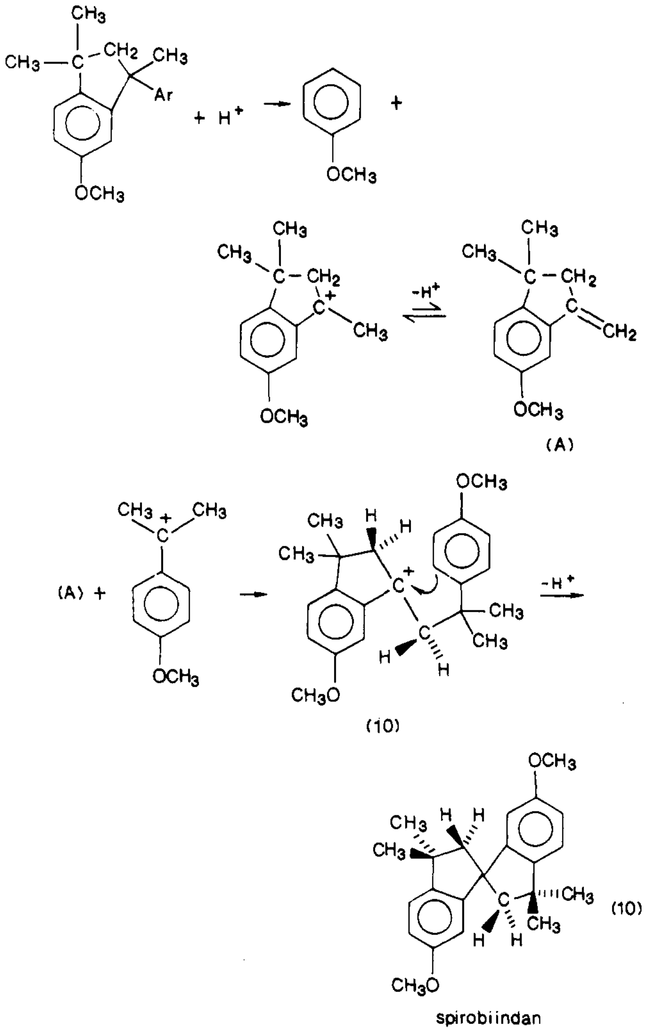


Figure 8. Same as Figures 3, 6, and 7: (a) after 60 min at 30 °C; (b) after reaction with methanol.

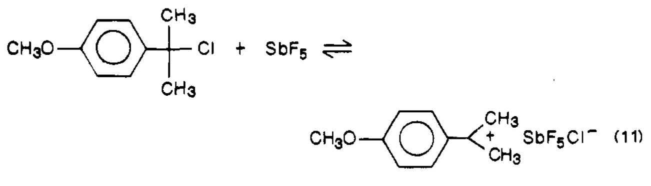
The reaction mixture corresponding to Figure 6 was still red. After a longer reaction time when both M_{3i}^+ and M_2^+ disappeared and only D_I and M_1^+ were present (Figure 7), the solution in the NMR tube became once again colorless. Thus the red color might be ascribed to the active centers M_2^+ or M_{3i}^+.

We found that the indan is not stable in the presence of the acid and of the monomeric cation. In experiments 2 and 4, where M_1^+ is present, spirobiindan and anisole are formed slowly at room temperature (Figure 8a). A similar reaction has been already described for unsubstituted α-methylstyrene.[15] See the chemical shifts for spirobiindan in Table I.



In Figure 8b may be observed the signals of the solvent CH_2Cl_2 (5.35 ppm), of the protonated terminating agent $CH_3OH_2^+$ (3.55 and 7.7 ppm) and of anisole [(3.80 (CH_3O), 7.30 (H_{meta}), and 6.90 ppm (H_{ortho} and H_{para})].

Ionization of the Tertiary Alkyl Chloride. We have described above the formation and the reactions of the cations derived from *p*-methoxy-α-methylstyrene by protonation using triflic acid. Another possibility for the synthesis of cations involves the ionization of the corresponding halide (*p*-methoxycumyl chloride) with a strong Lewis acid such as SbF_5



This reaction is strongly shifted to the right-hand side even for the unsubstituted cumyl chloride. According to Arnett[16] the latter reaction is very exothermic (ΔH = −19

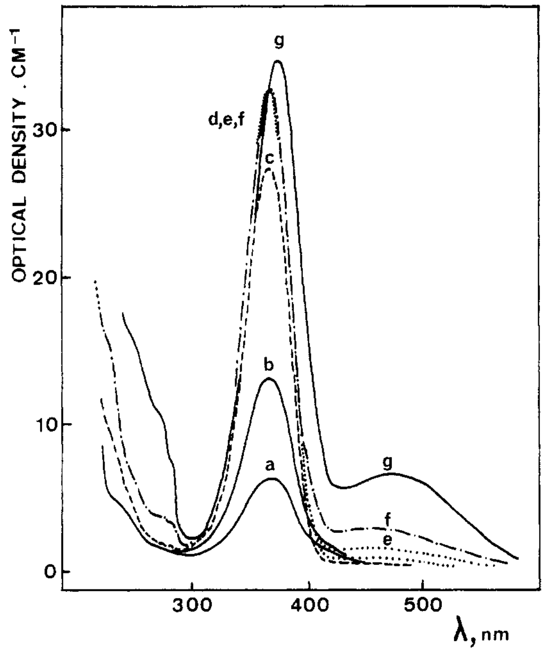


Figure 9. UV–visible spectra (at constant volume V_0 (−72 °C) = 27 mL) of the α-methyl-*p*-methoxystyrene/CF_3SO_3H system in dichloromethane at −72 °C (experiment UV_1). $[HA]_0 = 2.1$ mM (6.84×10^{-5} mol). $[M]_0/[HA]_0$: (a) 0.1; (b) 0.266; (c) 0.45; (d) 0.614; (e) 0.79; (f) 0.96; (g) 2.23.

kcal·mol^{-1}). The *p*-methoxy group should increase the stability of the cation. An experimental problem is, however, the instability of cumyl chlorides. The unsubstituted cumyl chloride decomposes slowly at low temperature and rapidly at ambient temperature. Only *p*-*tert*-butylcumyl chloride seems to be much more stable, but this might be ascribed to its crystalline structure.[20] The *p*-methoxy derivative decomposes rapidly in CH_2Cl_2, but it is more stable in the less polar $CHCl_3$. The rate constant of the decomposition of *p*-methoxycumyl chloride in $CDCl_3$ calculated as a unimolecular process is equal to 1.3×10^{-6} s^{-1} at 20 °C. Thus even after 1 h only a small fraction of the chloride is decomposed. Nevertheless the purity of the used chloride was only 92%. The main impurity was the chloride of the corresponding linear dimer. When this crude product was used for generation of the cation at −78 °C in CD_2Cl_2 solvent with SbF_5 first M_1^+ and small proportions of M_2^+ and of unreacted chloride were observed. However with progress of the reaction the relative proportion of M_1^+ decreased whereas those of M_2^+ (also M_{3i}^+) and of the chloride increased.

This could be the consequence of a slow reaction between nonassociated SbF_5 and monomer and to a shift of the equilibrium (11) to the left-hand side. Indeed, when monomer was reacted with SbF_5 alone the usual active species M_2^+ and M_{3i}^+ were observed. In a similar way $SbCl_5$ was reported to react with 1,1-diphenylethylene.[17]

It is possible that the dimeric cation formed from the dimer chloride (impurity always present) led to a rapid equilibration between free monomer, M_2^+ and M_{3i}^+. Free monomer, although present in a minute amount, could react with SbF_5, leading to the discussed shift in the equilibrium in eq 11. When a pure crystalline chloride was used in the case of *p*-*tert*-butylcumyl chloride the monomeric cation formed with SbF_5 was stable up to 0 °C.[20]

UV Studies. The ^1H NMR studies provided us with the following information:

1. Carbenium cations M_1^+, M_2^+, and M_{3i}^+ are stable at −63 °C. Above −40 °C, indan is formed that is slowly converted at room temperature into spirobiindan.

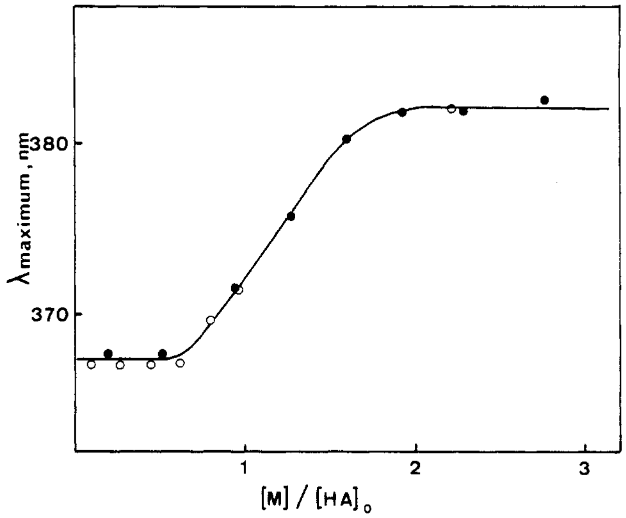


Figure 10. Dependence of the wavelength of the maximum of absorption on $[M]_0/[HA]_0$ ratios: (○) experiment UV_1, (●) experiment UV_2 ($[HA]_0 = 2.3$ mM, (6.95×10^{-5} mol)).

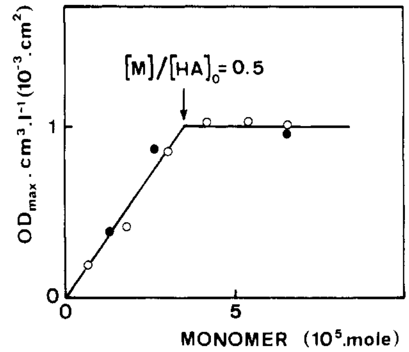


Figure 11. Determination of the extinction coefficient of the monomeric cation at 367.5 nm: (○) experiment UV_1; (●) experiment UV_2.

2. For $[M]_0 \leq {}^1/_2[HA]_0$ only M_1^+ is observed.
3. For ${}^1/_2[HA]_0 < [M]_0 < {}^3/_2[HA]_0$, cations M_1^+, M_2^+, and M_{3i}^+ coexist, their proportion depending on the $[M]_0/[HA]_0$ ratio.
4. For $[M]_0 > {}^3/_2[HA]_0$, M_2^+ and M_{3i}^+ are observed but with a ratio $[M]_0/[HA]_0 > 2$ only M_{3i}^+ (or M_{ni}^+) is present (and eventually ethylenic dimers).
5. When only M_1^+ is observed, the solution is colorless but in the presence of M_2^+ and M_{3i}^+, red color appears, which becomes dark red when only M_{3i}^+ is present.

To understand the change of color and to characterize the species in terms of the absorption maxima and extinction coefficients, we have carried out over the same range of concentration as for NMR, UV measurements at −72 °C for different $[M]_0/[HA]_0$ ratios.

In Figure 9 are shown typical spectra. For ratios $[M]_0/[HA]_0 < 0.61$ only one maximum at 367.5 nm is observed (see curves a–c). Neither monomer nor acid absorb above 300 nm at the used concentration. Above this ratio, a continuous bathochromic shift of the maximum is observed up to a ratio of 2 (Figure 10) and a new broad band appears (maximum at 460–480 nm). The ^1H NMR studies have shown that only M_1^+ is present for $[M]_0/[HA]_0 \leq 0.5$. In this range, the optical density increases linearly with the added quantity of monomer (Figure 11). At ratios >0.5, the optical density does not increase, indicating the HA_2^- structure of the counterion of M_1^+ and confirming the NMR results. From the slope of the curve in Figure 11, we may calculate the extinction coefficient of M_1^+ TfO^-, TfOH to be equal to $\epsilon = 28\,500$ L·mol^{-1}·cm^{-1}.

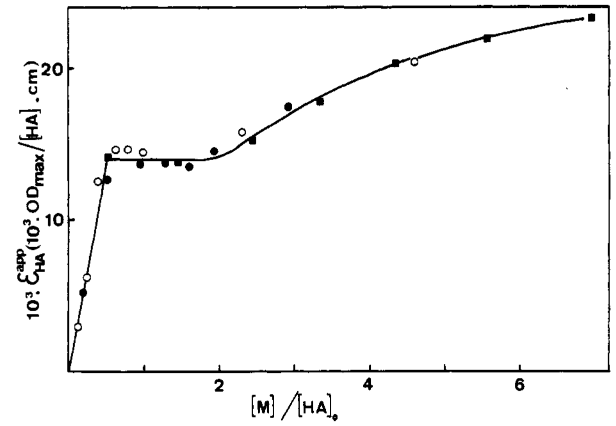


Figure 12. Dependence of the apparent extinction coefficient (calculated from the acid used) of the cationic species on the $[M]_0/[HA]_0$ ratios: (○) experiment UV_1; (●) experiment UV_2; (■) experiment UV_3 ($[HA]_0$ = 2.7 mM (7.39×10^{-5} mol)).

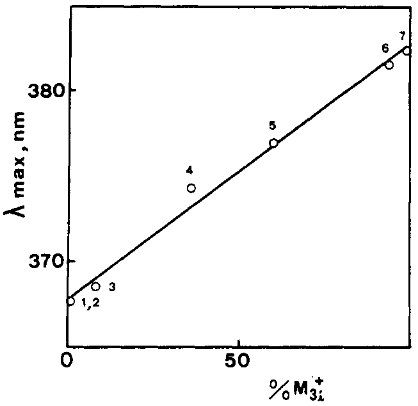


Figure 13. Correlation between the bathochromic shift of the main absorption and the proportion of M_{3i}^+ determined by ^1H NMR at the same ratios ρ (see Table II).

For $[M]_0 < {}^1/_2[HA]_0$, the excess of acid might exchange with HA_2^- and form the $H_2A_3^-$ anion as with 1,1-diphenylethylene.[3]

In the range ${}^1/_2[HA]_0 < [M] < {}^3/_2[HA]_0$ (Figure 12) the constant value of the apparent extinction coefficient $\epsilon_{[HA]}^{app}$ (calculated from the acid used) confirms the HA_2^- structure for the counterion of M_2^+ and M_{3i}^+. With the value of 14000 for $\epsilon_{[HA]}^{app}$ the extinction coefficient for M_2^+ and M_{3i}^+ was found equal to 28000.

This value may be compared with $\epsilon \geq 28000$ for *p*-methoxystyrene,[18,19] with $\epsilon = 35000$ for *p*-*tert*-butyl-α-methylstyrene[20] and with $\epsilon = 30000$ for *p*-isopropyl-α-methylstyrene,[9] if we suppose for this monomer the HA_2^- structure for the anion.

We have observed in NMR an increase of the proportion of M_{3i}^+ with the ratio $[M]_0/[HA]_0$ (up to 1.5–2.0). The good correlation between the proportion of M_{3i}^+ determined by NMR and the bathochromic shift observed in UV for the same ratio (Figure 13) suggests that the absorption band at 382.5 nm results from the M_{3i}^+ species and that the variation of λ_{max} is linked to the equilibria between M_1^+, M_2^+, and M_{3i}^+ (M_2^+ absorbing at the same maximum wavelength as M_1^+).

A bathochromic shift is also observed for the second broad band that varies from 460 to 478 nm and increases with $\rho = [M]/[HA]_0$. This increase of the optical density at 460–478 nm, varying linearly with the bathochromic shift of the main absorption band, may indicate that this band also is associated with the isomerized species (Figure 14).

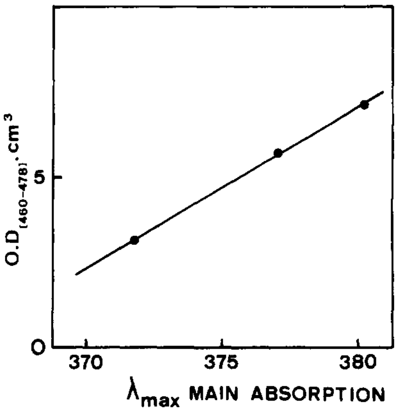


Figure 14. Dependence of the enhancement of the second absorption band on the bathochromic shift of the main absorption.

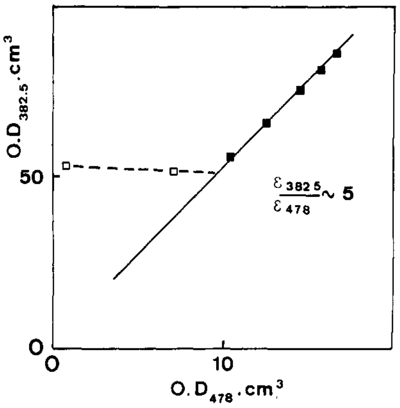


Figure 15. Variation of the optical density of the two maxima (experiment UV_3). $\rho < 1.5$ (□) 0.515, (measured at 367.5 and 460 nm), 1.46 (at 378 and 472 nm); $\rho > 1.5$ (■) 2.46, 3.37, 4.37, 5.56, 6.95 (measured at 382.5 and 478 nm).

New monomer additions (with $\rho > 1.5$) lead to an enhancement of the two maxima at 382.5 and 478 nm. This might be explained by initiation involving the acid present in the counterion with a simultaneous change of the structure of this anion from HA_2^- to A^- (cf. eq 12). For the quantitative conversion to A^-, $\epsilon_{[HA]}^{app}$ should reach a value of 28000 L·mol^{-1}·cm^{-1} for ρ equal to 3, but the real values are lower (see Figure 12). It is due to simultaneous monomer consumption and formation of ethylenic dimers (endo and exo) or trimer by transfer and tetrameric cations. This was verified by the GPC analysis of the final products (experiment UV3). It showed the presence of ethylenic trimers and dimers and small quantities of tetramer.

The tetrameric cations (as isomerized form) might be formed by a new addition of monomer to the linear trimeric cation (in equilibrium with M_{3i}^+) and isomerization or by addition of the dimeric cation to the exo ethylenic dimer

$$M_{3i}^+HA_2^- \xrightarrow{+M} M_{3i}^+A^- + M^+A^- \xrightleftharpoons{+M} M_{3i}^+A^- + M_2^+A^-$$

$$M_2^+A^- + D_E(\text{exo}) \rightarrow M_{4i}^+, A^- \qquad (12)$$

The isomerized cation (M_i^+) cannot react with the monomer at the C^+ center because the branched species would have too large steric hindrances. Apparently, the steric effects prevent also the growing cations from the reaction with the endo olefins.

The constant value of the optical density measured for the main absorption band (367.5–382.5 nm) for ratios $0.5 < \rho < 1.5$ is explained by the constant quantity of carbocations (M_1^+, M_2^+, and M_{3i}^+). In Figure 15 (broken line) is shown the increase of the absorption at the higher wavelength (460–478 nm). For ratios $[M]/[HA]_0 > 3$, more carbocations are formed, and the increase of the optical density at 478 nm is proportional to that of the first maximum at 382.5 nm. This observation confirms that these two absorption bands correspond to the isomerized species (M_{3i}^+ or M_{ni}^+). If this is assumed the extinction coefficient at 478 nm is found to be equal to 5600 $L\cdot mol^{-1}\cdot cm^{-1}$.

In a following article we shall report on the cationic polymerization of *p-tert*-butyl-α-methylstyrene, *p*-methyl-α-methylstyrene, and α-methylstyrene and compare them with *p*-methoxy-α-methylstyrene.[20]

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New Electrophilic Olefin Initiators for Cationic Polymerization

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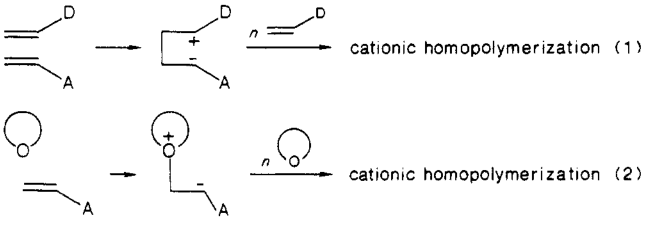
ABSTRACT: Four electrophilic olefins containing β-*p*-toluenesulfonate or β-trifluoroacetate groups were synthesized as new initiators for cationic polymerizations. These were 2,2-dicyanovinyl *p*-toluenesulfonate (**1**), 2-cyano-2-carbomethoxyvinyl *p*-toluenesulfonate (**2**), 2,2-dicyanovinyl trifluoroacetate (**3**), and 2-cyano-2-carbomethoxyvinyl trifluoroacetate (**4**). They function by forming zwitterionic intermediates which expel the leaving group to form a carbenium–gegenion pair. They were active initiators for the cationic polymerization of electron-rich vinyl monomers and oxacyclic monomers. Moreover, **1** and **2** but not **3** and **4** displayed suitable stability by being insensitive to water, thus excluding adventitious polymerizations by *p*-toluenesulfonic acid.

Introduction

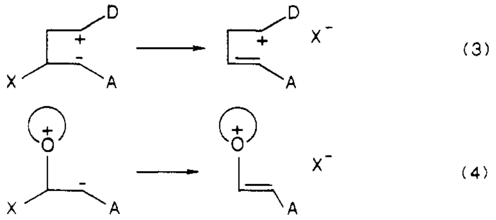
In past research we have shown that electrophilic multisubstituted ethylenes can initiate cationic vinyl and ring-opening polymerizations by forming reactive zwitterions with the monomers.[1] These zwitterions are the true initiating species.[2,3]



D = donor substituent
A = one to four acceptor substituents

However, the presence of the carbanion center limits such cationic polymerizations to those of the most electron-rich monomers.

The efficiency of such zwitterionic initiators was greatly increased if they possessed a leaving group at the β-position.[3-5] Its expulsion leaves a carbenium–gegenion pair which initiates and propagates more effectively.



The choice of the leaving group X in these initiators requires careful consideration. First, the monomer must be more nucleophilic than X^-, or high polymer cannot be formed. When X was Cl^- or I^-, the very electron-rich monomers *N*-vinylcarbazole and *N*-ethyl-3-vinylcarbazole polymerized successfully, but the less nucleophilic *p*-methoxystyrene gave only low polymers.[4,6] Chloride ion also interfered with 1,3-dioxolane.[3] In this latter case, 1,3-dioxolane polymerization initiated by β,β-dicyanovinyl chloride, oligomers could be isolated in which the presence of the head group (dicyanovinyl) and end group (chloride) was proven by NMR spectroscopy.

When X was $^-O_3SCF_3$ (triflate), *p*-methoxystyrene, trioxane, and tetrahydrofuran could be polymerized successfully, but now another complication arose.[5] The initiators β,β-dicyanovinyl triflate and tricyanovinyl triflate