Macromolecules 1987, *20*, 2679-2689

Active Centers in the Cationic Polymerization of α-Methylstyrenes. 2. *p-tert*-Butyl, *p*-Methyl, and Unsubstituted α-Methylstyrene. Comparison with *p*-Methoxy-α-methylstyrene†

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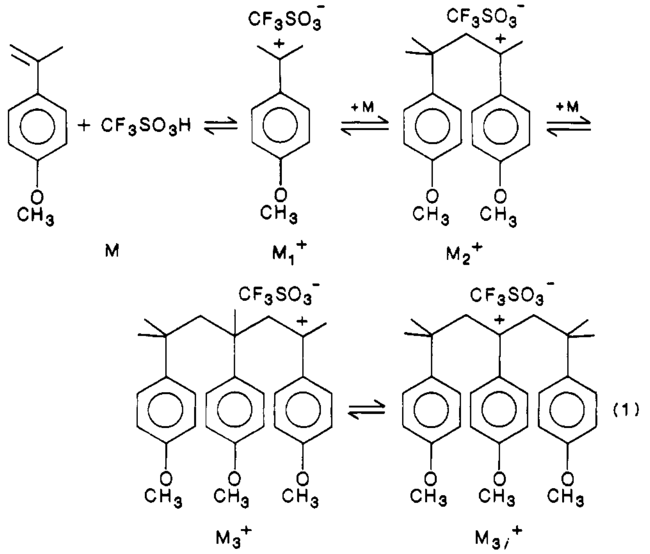
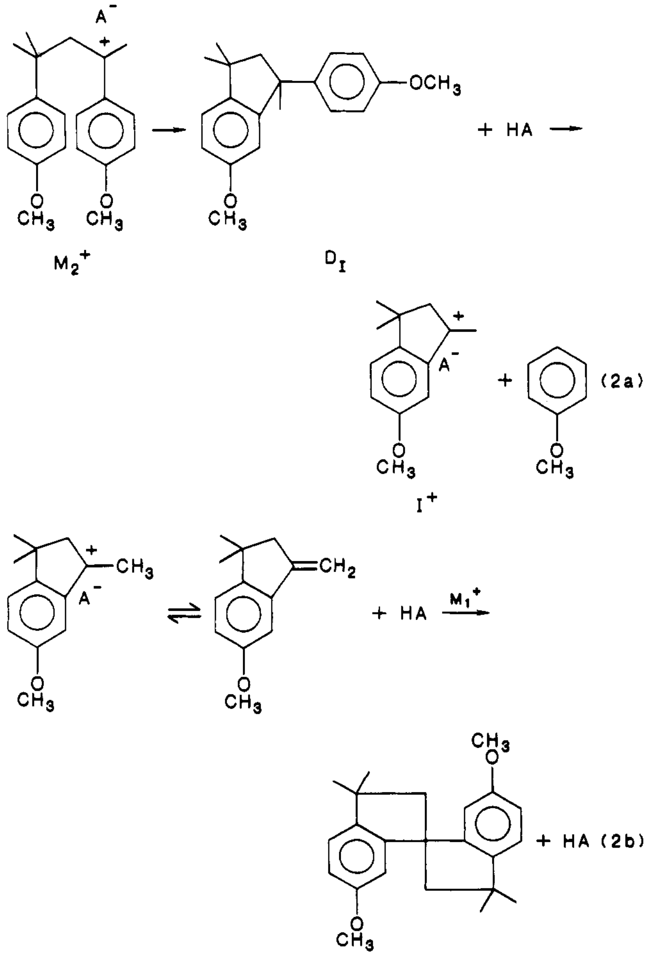
ABSTRACT: Carbocationic species derived from different α-methylstyrenes, i.e. *p-tert*-butyl-α-methylstyrene (BMS), *p*,α-dimethylstyrene (DMS), and α-methylstyrene (MS), have been studied by ^1H NMR spectroscopy and correlated with UV spectra. Carbenium ions were generated by the addition of trifluoromethanesulfonic (triflic) acid to the solutions of monomeric or dimeric olefins and by the reaction of the para-substituted cumyl chlorides with SbF_5. These results are compared with those reported for *p*-methoxy-α-methylstyrene (MOMS). Monomeric cations ($ArC(CH_3)_2^+$) are stable below −70 °C in CH_2Cl_2 solvent. The cation derived from SbF_5 and chloride for BMS is stable up to 0 °C. In contrast to MOMS, dimeric and trimeric cations are unstable and cyclize rapidly to form indan derivatives which are converted into indanyl cations above 0 °C. Monomeric cations show a strong absorption at about 350 nm with the extinction coefficient $\epsilon \approx 30000$, i.e. much higher than previously observed in superacid media. In the presence of an excess of monomer a bathochromic shift (~15 nm) of the main maximum and the appearance of a new maximum (~480 nm) were observed. This indicates either internal complexation of the carbocations with aromatic nuclei from its own chain (isomerized species) or external complexation with monomer and linear olefins. The thermodynamics, kinetics, and chemistry of elementary reactions involved in cationic polymerization of α-methylstyrenes are discussed.

1. Introduction

In a previous paper[1] we described the results of our studies of the structure of active centers in the cationic polymerization of *p*-methoxy-α-methylstyrene (MOMS). We have found that in CH_2Cl_2 at −63 °C with use of equimolar amounts of triflic acid and monomer, the corresponding monomeric cation (M_1^+), dimeric cation (M_2^+), and trimeric cation are in dynamic equilibria. The trimeric cation exists primarily as the isomerized structure M_{3i}^+ and not as M_3^+ (eq 1).



The lifetime of the above cations at $T < -60$ °C is very long, and no decomposition is observed for a few weeks. The exchange between the different cations is, on the other hand, slower than the NMR time scale so they can be observed as separate species. At higher temperatures the indan-type dimer (D_I) starts to form. This dimer, in the presence of acid, gives the indanyl cation (I^+) which at room temperature and in the presence of the monomeric cation is eventually converted into spirobiindan (eq 2).



At a higher $[M]_0/[HA]_0$ ratio either the polymer or the mixture of linear unsaturated oligomers is formed. The

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† Part 1: see ref 1.

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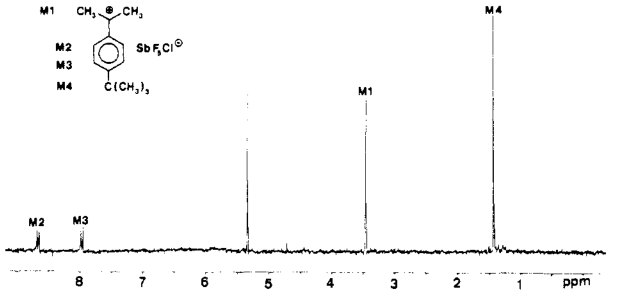


Figure 1. 250-MHz ^1H NMR spectrum of *p-tert*-butylcumyl chloride ($[RCl]_0 = 0.015$ mol/L) after reaction with $[SbF_5]_0 = 0.015$ mol/L in CD_2Cl_2 at -70 °C.

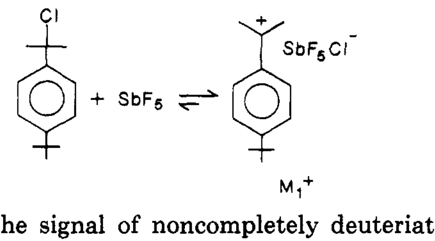
isomerized active centers are present.

The *p*-methoxy group stabilizes carbocations and prevents cyclization by the decrease of the electron density in its meta position (slowing down indan formation). It is interesting to compare the behavior of this monomer with those of unsubstituted and *p*-alkyl-substituted α-methylstyrenes. In this paper we shall discuss the ^1H NMR and UV spectra of cations derived from *p-tert*-butyl-α-methylstyrene (BMS), *p*,α-dimethylstyrene (DMS), and unsubstituted α-methylstyrene (MS). These cations were formed either by ionization of the corresponding chlorides in the presence of SbF_5 or by the reaction between monomers and trifluoromethanesulfonic acid. We shall first give the results of our ^1H NMR and UV studies and then discuss the structure and behavior of these cations in comparison with the cations derived from *p*-methoxy-α-methylstyrene (MOMS). We shall also discuss some results already reported on the polymerization of *p*-isopropyl-α-methylstyrene (PMS).[2]

2. Results

2.1. ^1H NMR Spectra. ^1H NMR spectra were recorded in deuteriated dichloromethane by using a 250-MHz spectrometer and tubes sealed under vacuum. The spectra were usually taken at low temperatures (-70 °C) just after homogenization of the reaction mixture.

2.1.1. *p-tert*-Butyl-α-methylstyrene (BMS). As stated in the Introduction, cations were formed either by the ionization of the halides or by protonation of the monomers. In Figure 1 the NMR spectrum of the cation formed by the first method is shown. The equimolar mixture of SbF_5 and *p-tert*-butyl-α,α-dimethyl benzyl chloride in CD_2Cl_2 solvent at -70 °C gives the monomeric carbenium cation M_1^+ with the complex anion SbF_5Cl^- (eq 3).

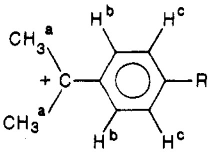


(3)

M_1^+

Besides the signal of noncompletely deuteriated dichloromethane at 5.35 ppm, the following absorptions are present: 8.67 (2 H, aromatic ortho protons), 7.97 (2 H, aromatic meta protons, $J_{om} = 8.9$ Hz), 3.46 (6 H, two methyl groups), and 1.44 ppm (9 H, *p-tert*-butyl group). This is a strong shift downfield in comparison with the intial chloride (respectively 7.51, 7.38 ($J = 8.6$ Hz) 1.97, and 1.28 ppm). This reaction mixture is surprisingly stable up to 0 °C.

Table I
^1H NMR Chemical Shifts[a] of Monomeric Cations (M_1^+) in CD_2Cl_2 at -70 °C



R	H^a	H^b	H^c	H(R)	J_{bc}, Hz
H	3.62	8.78	8.02	8.62	8.4
CH_3	3.44	8.63	7.79	2.80	8.6
$C(CH_3)_3$	3.46	8.67	7.97	1.44	8.9
OCH_3	3.04	8.60	7.31	4.31	9.2

[a] Using as reference the chemical shift of CH_2Cl_2 (δ 5.35).

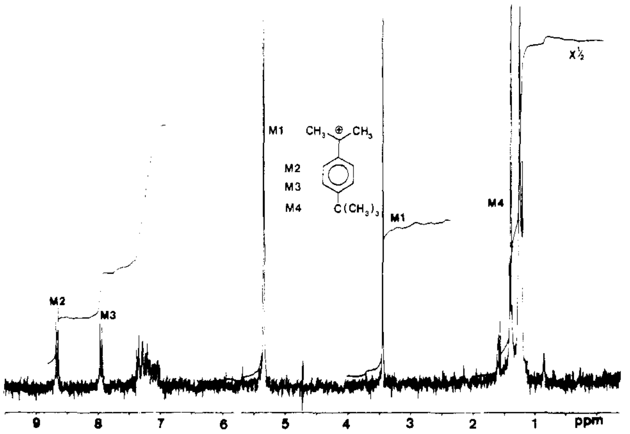


Figure 2. 250-MHz ^1H NMR spectrum of *p-tert*-butylcumyl chloride ($[RCl]_0 = 0.015$ mol/L), after reaction with $[SbF_5]_0 = 0.015$ mol/L and $[BMS]_0 = 0.015$ mol/L after 10 min at -70 °C in CD_2Cl_2.

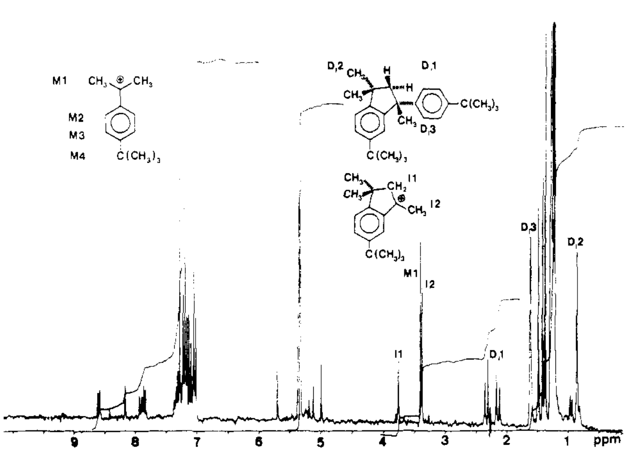


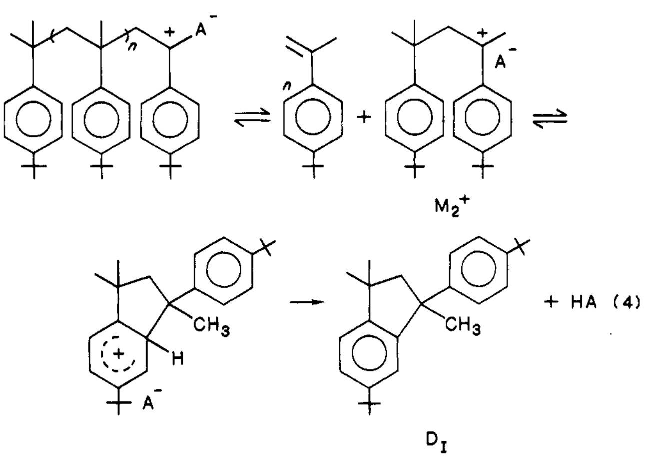
Figure 3. The same as Figure 2 but after 2 days at -20 °C.

The ^1H NMR spectrum of an equimolar mixture of SbF_5, chloride and monomer at -70 °C is shown in Figure 2. In addition to the previously discussed signals of the monomeric cation, the absorptions of some oligomeric products appear (aromatic protons at 7.40–7.05 ppm, aliphatic at 1.60–0.86 ppm).

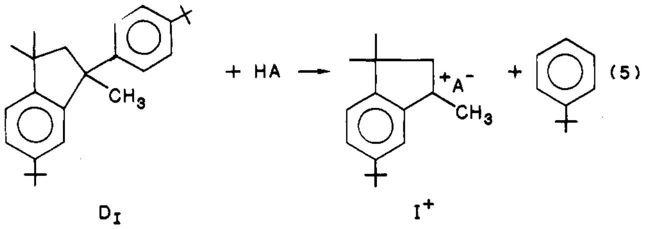
After a longer reaction time (e.g. 2 days, see Figure 3) these oligomers form an indan-type dimer (D_I) with a characteristic AB pattern for the methylene group at 2.4–2.1 ppm (cf. Table II).

This reaction might proceed by deprotonation of higher oligomers to M_2^+ capable of rapid cyclization (eq 4).

The last step (proton abstraction) probably proceeds with the assistance of some basic reagent (e.g. monomer) because the basicity of SbF_5Cl^- is too low to take part in this reaction (cf. Discussion). The concentration of the intermediate cation M_2^+ is too low to be directly observed in the NMR spectrum.

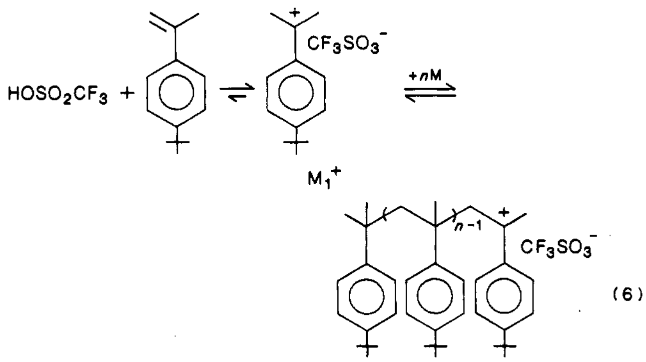


The indan-type dimer is at a later stage converted into indanyl cation (I^+) by expulsion of the aromatic ring (eq 5).



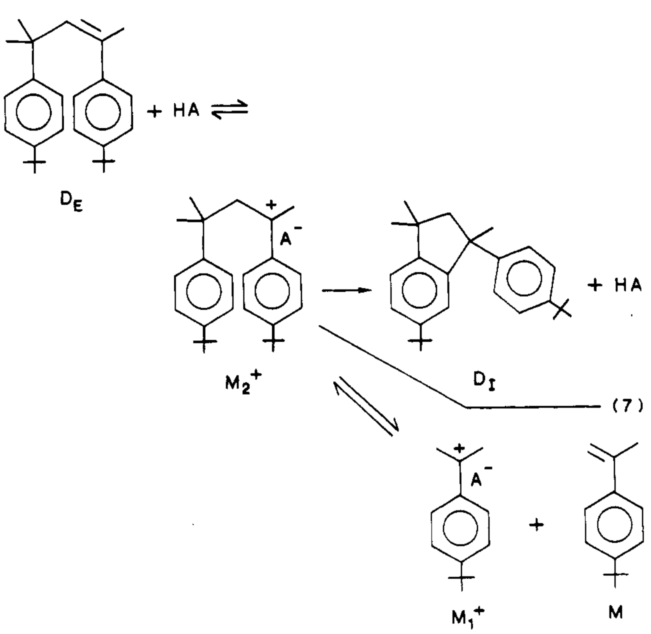
M_1^+, D_I, and I^+ were identified in Figure 3 (cf. Tables I–III for the assignments of all protons).

Cations have also been generated by direct reaction between the acid and the monomer (eq 6).



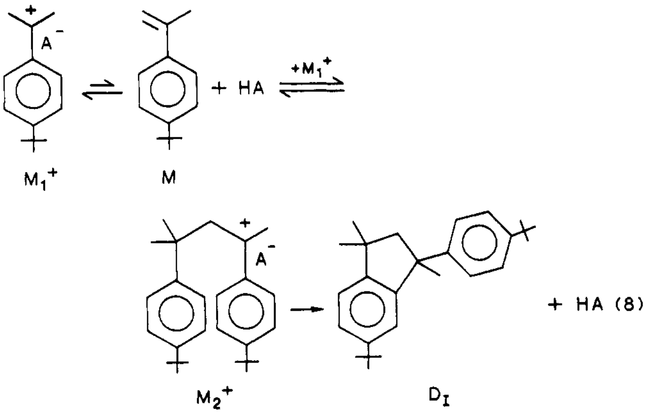
An equimolar mixture of triflic acid and monomer ($[HO_3SCF_3]_0 = [M]_0 \approx 4 \times 10^{-2}$ mol/L) gave at −70 °C about 25% of M_1^+ and 75% of some oligomerics. This indicates that the rate constants of protonation is lower than that of propagation. During the first minutes no indan-type dimer was formed. This dimer appears later and is probably due to depropagation of the longer chains to M_2^+ (cf. eq 4). At higher temperatures various indanyl cations are formed, and the reaction shown in eq 5 dominates.

Thus, in contrast to MOMS we could directly observe neither M_2^+ nor M_3^+. The synthesis of M_2^+ was attempted by the direct protonation of the endo linear ethylenic dimer (D_E). At −78 °C after the acid was mixed with D_E, a transient orange color appeared, but in the spectrum taken after fewer than 2 min, only M_1^+ and D_I were identified. This reaction probably proceeds by eq 7.



The transient orange color may be ascribed either to M_2^+ (or higher cations formed with M), to isomerized cations M_i^+, or to complexes between any carbenium cation and an olefin (M or D_E). When D_I is formed, the acid reacts with an olefin leading eventually to the colorless cation M_1^+.

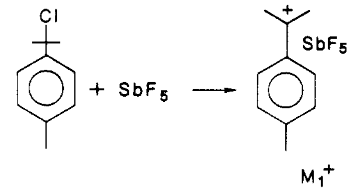
M_1^+ was slowly converted into D_I at −70 °C ($k_{-i} \approx 10^{-4}$ s^{-1}). This reaction may involve deprotonation of M_1^+ and the reaction of the remaining M_1^+ with the liberated monomer to form M_2^+ which rapidly cyclizes to D_I (eq 8).



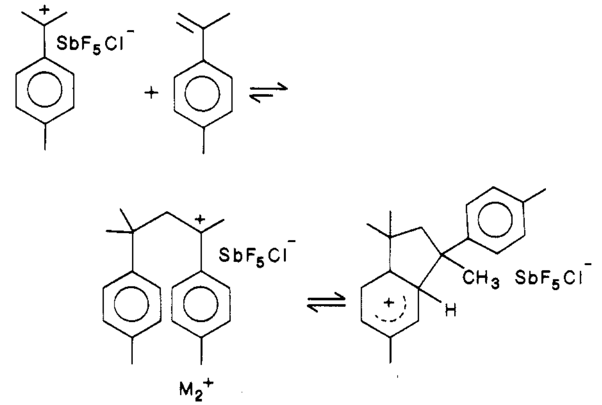
This reaction occurs only with the relatively basic trifluoromethanesulfonic anion. The monomeric cation associated with the complex nonbasic counteranion SbF_5Cl^- is stable at temperatures up to 0 °C.

2.1.2. *p*,α-Dimethylstyrene (DMS). Cumyl chlorides are known to decompose rapidly even at room temperature. The *p*-*tert*-butyl derivative discussed in the previous section is an exception because it crystallizes easily and has a higher stability in its crystalline form. Freshly distilled *p*-methylcumyl chloride (bp 48 °C, 0.001 mm) contains approximately 5–10% of olefins (monomer, exo and endo linear dimers). Reactions of such a crude chloride with SbF_5 in CD_2Cl_2 at −70 °C leads to M_1^+ and to indan-type dimer (D_I) by formation of the transient M_2^+ and rapid cyclization (eq 9).

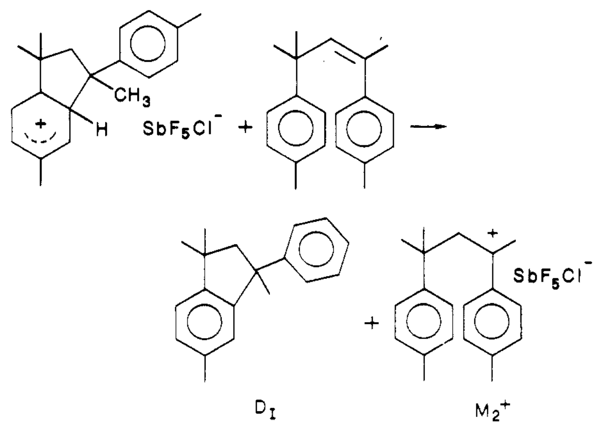
As already mentioned the anion SbF_5Cl^- is not basic enough to abstract a proton to form the indan-type dimer D_I. The participation of an olefin (monomer or dimer) is required. In Figure 4 the ^1H NMR spectrum of the reaction mixture is shown. The aromatic protons of M_1^+ absorb at 8.63 (ortho) and 7.79 ppm (meta), α-methyl groups absorb at 3.44 ppm, and a *p*-methyl group at 2.80 ppm. A small shift upfield is noticed in comparison with BMS. Three methyl groups of D_I absorb at 0.93, 1.26, and 1.58 ppm. The methylene group produces an AB pattern



(9a)



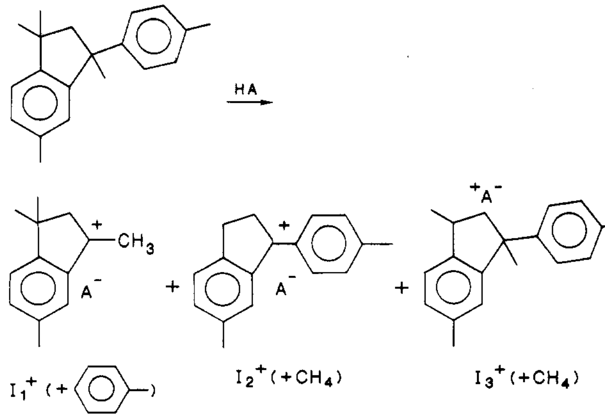
(9b)



(9c)

(2.18 and 2.34 ppm, J = 13 Hz), and the *p*-methyl groups absorb at 2.30 and 2.25 ppm.

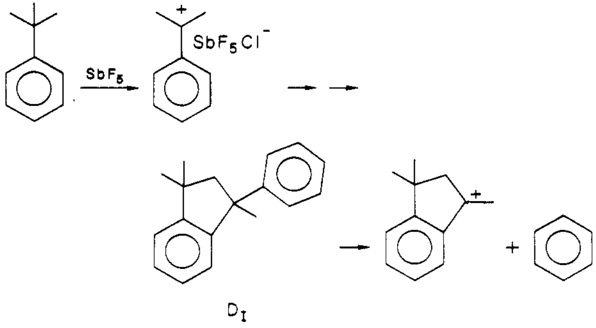
The reaction between equimolar amounts of monomer and triflic acid ($[M]_0 = [CF_3SO_3H] \approx 4 \times 10^{-2}$ mol/L) leads to predominant indan formation even at −70 °C. The yield of M_1^+ is lower than for BMS and does not exceed 15%. At higher temperatures the indan is eventually converted into indanyl cations I_1^+, I_2^+, and I_3^+ (eq 10).



(10)

The cation formed by the expulsion of toluene (I_1^+) prevails, the lowest concentration being I_3^+. Indanyl cations with *p*-alkyl substituents are stable under vacuum at room temperature and decompose slowly in open systems. In contrast to MOMS, indanyl cations do not form spirobiindan compounds.

2.1.3. α-Methylstyrene (MS). Cumyl chloride reacts with SbF_5 yielding M_1^+, an indan dimer (D_I), and some oligomeric products. At room temperature the reaction mixture eventually yields benzene and indanyl cations (eq 11).



(11)

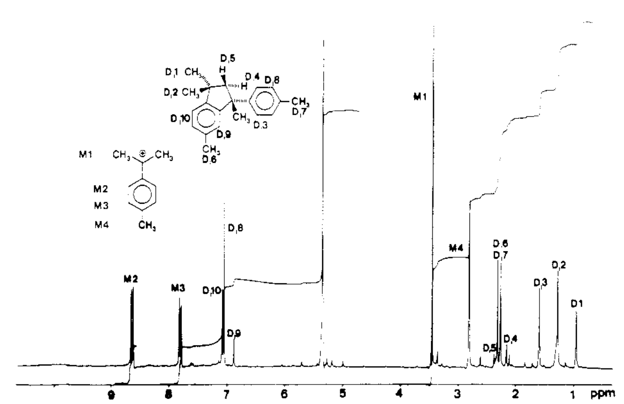


Figure 4. 250-MHz ^1H NMR spectrum of *p*-methylcumyl chloride ($[RCl]_0$ = 0.020 mol/L) after reaction with $[SbF_5]_0$ = 0.020 mol/L at −70 °C in CD_2Cl_2.

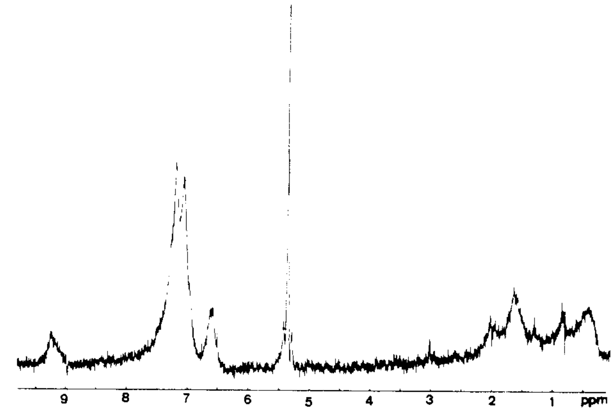


Figure 5. 250-MHz ^1H NMR spectrum of $[MS]_0$ = 0.05 mol/L after reaction with $[CF_3SO_3H]_0$ = 0.05 mol/L in CD_2Cl_2 at −70 °C after 5 min.

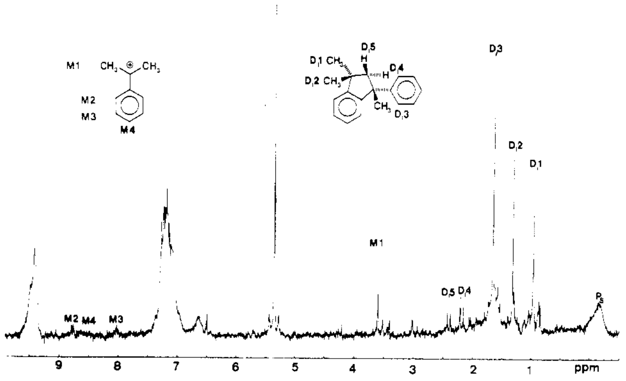
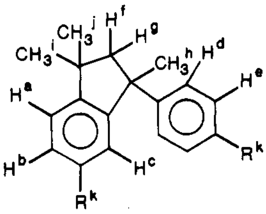


Figure 6. The same as Figure 5 but at −40 °C after 10 min.

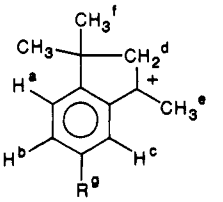
Table II
^{1}H NMR Chemical Shifts^a of Indans in CD_2Cl_2 at -70 °C



R	H^a	H^b	H^c	H^d	H^e	H^f	H^g	H^h	H^i	H^j	H^k		J_{AB}, Hz	J_{BC}, Hz	J_{DE}, Hz	J_{FG}, Hz
H	*b*	*b*	*b*	*b*	*b*	2.38	2.17	1.63	1.29	0.92	*b*	*b*				13.0
CH_3	7.08	7.08	6.87	7.04	7.04	2.34	2.12	1.58	1.26	0.93	2.30	2.2				13.0
$C(CH_3)_3$	7.12	7.29	7.17	7.03	7.22	2.32	2.13	1.60	1.22	0.85	1.27	1.2	8	1.5	8.4	12.9
OCH_3	7.12	6.86	6.65	7.08	6.79	2.32	2.15	1.60	1.26	0.91	3.83	3.7	11	2.5	8.7	12.5

[a] Using as the reference the chemical shift of CH_2Cl_2 (5.35 ppm). [b] Multiplet in the region 7.30–7.10 ppm.

Table III
^{1}H NMR Chemical Shifts^a of Indanyl Cations in CD_2Cl_2 at -70 °C



R	H^a	H^b	H^c	H^d	H^e	H^f	H^g
H	7.90	8.60	8.50	3.87	3.58	1.60	7.90
CH_3	7.92	8.51	8.30	3.85	3.44	1.58	2.63
$C(CH_3)_3$	7.87	8.67	8.18	3.76	3.37	1.47	1.36

[a] Using as reference the chemical shift of CH_2Cl_2 (5.35 ppm).

Table IV
UV Absorption Maxima and Extinction Coefficients of Cationic Species in CH_2Cl_2 at -72 °C

	M_1^+		M_i^+			
R	λ, nm	ϵ	λ_1, nm	ϵ_1	λ_2, nm	ϵ_2
H	333	>26 300				
CH_3	345	>12 300	358	>22 000	480	>6000
$C(CH_3)_3$	350	35 000	363	>22 600	490	>6100
OCH_3[a]	368	28 500	382	28 000	478	>6000

[a] Reference 1.

Reaction between monomer and the acid ($[M]_0 = [HO_3SCF_3]_0 \approx 5 \times 10^{-2}$ mol/L) at −70 °C in CD_2Cl_2 gives oligomeric and polymeric products (Figure 5). The proton of the unreacted acid absorbs at 9.2 ppm. At a higher temperature (−40 °C) the monomer equilibrium concentration increases and polymer depropagates (cf. Discussion). In the spectrum (Figure 6), a small proportion of polymer (around 0.2 ppm: syndiotactic structure)[3] has been found. At the same time indan is formed (δ_A 2.39, δ_B 2.18, J_{AB} = 13 Hz) and the monomeric cation M_1^+ appears (α-methyl groups absorb at 3.62 ppm). The signal of the acidic protons shifts slightly downfield (δ 9.41) due to the exchange with anions $CF_3SO_3^-$.[4] However, the proportion of the monomeric cation is very low (3% from the used acid). Later, only the indan and the indanyl cations were observed.

2.2. Ultraviolet–Visible Spectroscopy. 2.2.1. *p*-*tert*-Butyl-α-methylstyrene. ^{1}H NMR studies indicate that the reaction between the *p*-*tert*-butyl-α,α-dimethylbenzyl chloride and SbF_5 leads quantitatively (see Figure 1) to M_1^+ (cf. eq 3). Therefore this system allows measurement of the absorption maxima and of the extinction coefficient of this cation. The addition of the precooled solution of the chloride under vacuum to the cold (−73 °C) solution of SbF_5 ($[RCl]_0 = 1.18 \times 10^{-3}$ mol/L, $[SbF_5]_0 = 1.91 \times 10^{-3}$ mol/L) gave a strong absorption at 350 nm, attributed to the cation. The apparent extinction coefficient, ϵ, of the cation calculated by assuming a 100% yield from the chloride was equal to 30 500.

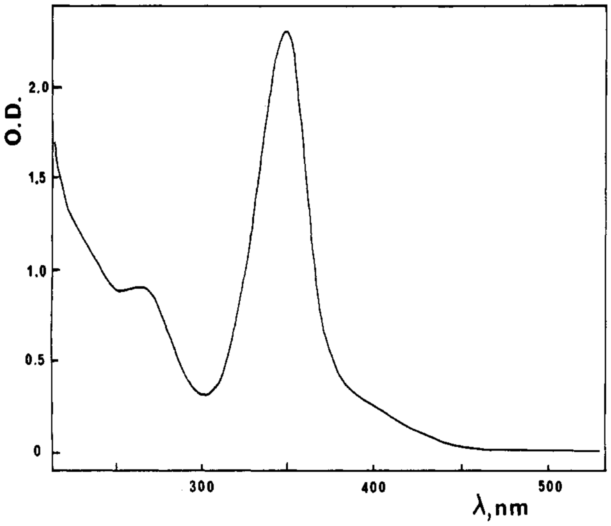


Figure 7. UV spectrum of *tert*-butylcumyl chloride ($[RCl]_0$ = 1.56×10^{-3} mol/L) after reaction with SbF_5 ($[SbF_5]_0 = 1.31 \times 10^{-3}$ mol/L) in CH_2Cl_2 at −73 °C.

The addition of a new portion of the chloride (see Figure 7) led to an increase of ϵ to 35 000, ϵ now being calculated by assuming a 100% yield of cation from SbF_5 ($[RCl]_0 = 1.56 \times 10^{-3}$ mol/L, $[SbF_5]_0 = 1.31 \times 10^{-3}$ mol/L). The latter value (ϵ = 35 000) seems to be more reliable because in solution part of the chloride might have decomposed, leading to a decrease of the real concentration of chloride (cf. Experimental Section).

The monomeric cation was also formed in the reaction between monomer and triflic acid ($[M]_0 = 5 \times 10^{-3}$ mol/L, $[HO_3SCF_3]_0 = 1.2 \times 10^{-3}$ mol/L). Besides the signal of the cation at 350 nm, two sharp maxima at $\lambda = 274$ and 265 nm were also observed. They are ascribed to D_I. The concentration of indan was estimated by using the extinction coefficient of the unsubstituted indan ($\epsilon = 1550^5$ and is equal to $[D_I] = 1.8 \times 10^{-3}$ mol/L). Thus the maximal concentration of monomer available to form the cation is still higher than the initial concentration of the acid ($[M]_0 - 2[D_I] = [M] > [HA]_0$, i.e. 1.4×10^{-3} mol/L > 1.2×10^{-3} mol/L). The extinction coefficient of the cation, assuming quantitative formation of M_1^+ from each acid molecule, is equal to 13 800 i.e., much less than the ϵ of the cation derived from the chloride. Usually the extinction coefficients of the ions do not depend on the counterion structure, although some bathochromic shift was noted for carbanions derived from styrene when the radii of the cations were significantly changed (e.g. Li^+, Na^+, K^+). In our system the λ_{max} is constant and we will assume that the real ϵ is also the same (i.e. $\epsilon = 35\,000$). The smaller value of the apparent ϵ may be ascribed to a lower than quantitative yield of cation based on the acid. Part of the monomer forms a polymer undetected by UV and part of the acid associates with the counterion. Such association have been previously observed in similar systems.[1,4]

In GPC traces of the reaction mixture quenched with sodium methanolate, about 20% was found to be oligomers with $M_n \simeq 1500$. The rest consists of species with $M_n \simeq 300$ (indan dimer) and species with $M_n \simeq 200$ (presumably products of the reaction of M_1^+ with CH_3O^-). The relative proportions are equal to 70% and 10%. This latter value is in agreement with the assumption of the similar values of ϵ (i.e. 35 000). The ^{1}H-NMR spectrum of the quenched reaction mixture indicates the presence of about 70% indan (AB pattern in the range 2.10–2.30 ppm).

When a smaller excess of monomer ($[M]_0 = 5.4 \times 10^{-4}$ mol/L) over acid ($[HA]_0 = 2.3 \times 10^{-4}$ mol/L, see Figure 8) was used (ratio $n = 2.4$, previously $n = 4.2$), the apparent ϵ value calculated assuming the quantitative formation of M_1^+ from each acid molecule was still lower ($\epsilon_{app} = 8700$ at $\lambda = 350$ nm). However, calculations of the indan concentration (band at $\lambda = 274$ nm) led to the value $[D_I] = 2.3 \times 10^{-4}$ mol/L which limits the maximum possible concentration of monomeric cation to $[M_1^+] < 0.8 \times 10^{-4}$ mol/L, i.e. nearly 3 times less than $[HA]_0$. This leads again to $\epsilon \simeq 35\,000$ and indicates an even stronger association of the acid with the anion. Thus, at a lower ratio of $[M]_0/[HA]_0$ the acid prefers to complex with its anion to form $CF_3SO_3H \cdot SO_3CF_3^-$; at a higher ratio, monomer might successfully compete with the anion to increase the yield of carbenium ions.

A larger excess of monomer was then added to the same reaction mixture at −73 °C ($[M]_0 = 5.9 \times 10^{-3}$ mol/L, $[HA]_0 = 1.5 \times 10^{-4}$ mol/L, $n = 38$). The colorless mixture turned orange, a new maximum appeared at 490 nm, and the maximum at 350 nm shifted to 363 nm (see broken line in Figure 8). The apparent extinction coefficients calculated assuming each acid molecule gives birth to a carbenium ion are equal to 22 600 ($\lambda = 363$ nm) and 6100 ($\lambda = 490$ nm). The spectrum did not change within 1 h at −73 °C.

Later a new solution of the acid ($[M]_0 = 4.5 \times 10^{-3}$ mol/L, $[HA]_0 = 2.3 \times 10^{-4}$ mol/L, $n = 19$) was added to the same mixture. An increase of absorption was noted for both peaks (see dotted lines, Figure 8). The apparent ϵ values recalculated for the quantitative formation of cations from each acid molecule did not change significantly: $\epsilon = 21\,700$ ($\lambda = 363$ nm) and $\epsilon = 5700$ ($\lambda = 490$ nm). This means there were olefins (monomer, linear dimer, or trimer) available for protonation in the system. This system is stable at −73 °C for at least 20 min. Warming the mixture form −73 to −62 °C leads to a rapid disappearance of the absorption at $\lambda = 250$ nm (monomer or linear dimer and trimer), increase of absorptions at 274 and 265 nm (indan), disappearance of the absorption at 490 nm, and an hypsochromic shift from 363 to 350 nm as well as the disappearance of the orange color (see Figure 9). The decrease of the maximum at 490 nm proceeds with an estimated rate constant of 10^{-2} s^{-1}.

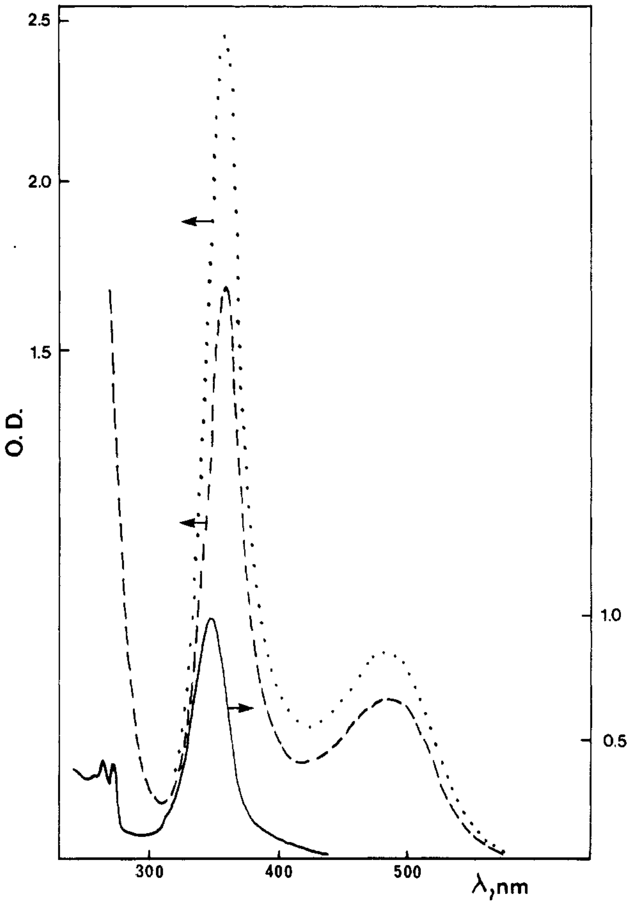


Figure 8. UV spectra in CH_2Cl_2 at −73 °C of the mixture: —, $[BMS]_0 = 5.4 \times 10^{-4}$ mol/L, $[CF_3SO_3H]_0 = 2.3 \times 10^{-4}$ mol/L; - - -, $[BMS]_0 = 5.9 \times 10^{-3}$ mol/L, $[CF_3SO_3H]_0 = 1.5 \times 10^{-4}$ mol/L; ···, $[BMS]_0 = 4.5 \times 10^{-3}$ mol/L, $[CF_3SO_3H]_0 = 2.3 \times 10^{-3}$ mol/L.

Later, a slow disappearance of the absorption at 350 nm (M_1^+) was observed ($k \simeq 10^{-4}$ s^{-1}). Eventually, at higher temperatures, a signal at 335 nm was formed. This may be ascribed to the indanyl cation (cf. eq 5).

The reaction between the acid and the linear dimer (endo) has been also studied. When the acid concentration was higher than that of the dimer ($[HA]_0 = 5 \times 10^{-3}$ mol/L, $[D_E] = 1.5 \times 10^{-3}$ mol/L), a very rapid formation of indan ($\lambda = 274$ and 265 nm) and M_1^+ ($\lambda = 350$ nm) was observed in agreement with the ^{1}H NMR studies. However, when a 15-fold excess of the dimer was used, the two maxima at 363 and 490 nm were formed. This mixture converted much more slowly, into D_I and M_1^+, indicating a stabilizing effect (complex formation?) of the olefin. After conversion of the olefins to indan derivatives, the second maximum disappeared and hypsochromic shift occurred.

2.2.2. *p*,α-Dimethylstyrene (DMS). Attempts to prepare M_1^+ in high yield from *p*,α,α-trimethylbenzyl

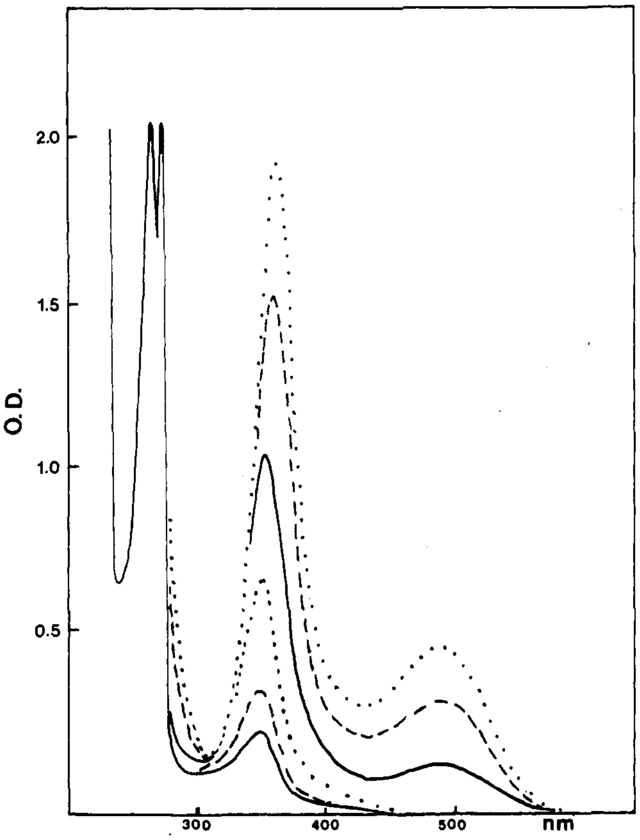
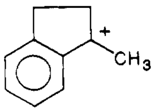
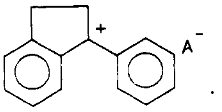


Figure 9. UV spectra in CH_2Cl_2 at −62 °C of the mixture $[BMS]_0 = 4.5 \times 10^{-3}$ mol/L and $[CF_3SO_3H]_0 = 2.3 \times 10^{-3}$ mol/L after (···) 1 min, (- - -) 2 min, (—) 5 min, (···) 8 min, (- - -) 15 min, and (—) 50 min.

chloride and SbF_5 were unsuccessful. NMR studies have already indicated a very low stability of the chloride in the pure state. CH_2Cl_2 solutions of the chloride decomposed even more rapidly. In the UV spectra of the 1:1 mixture of SbF_5 and chloride at −73 °C two maxima were observed, one at 326 nm with a shoulder at 345 nm and a much weaker one at 420 nm. The absorption at 326 nm was ascribed to the indanyl cation I_1^+ (cf. eq 10). We have prepared this cation independently, and it showed an absorption at 325 nm (ϵ = 26 700). These values may be compared with those of the 1-methylindan-1-ylium cation, absorbing at 318 nm (ϵ = 28 000).[6]



The absorption at 420 nm is attributed to the cation I_2^+ (cf. eq 10). A similar cation described in literature, the 1-phenylindan-1-ylium



cation has a maximum at 414 nm (ϵ = 32 000)[6] ($CF_3SO_3^-$ counterion, CH_2Cl_2, −70 °C) or at 412 nm (ϵ = 37 000)[6] (HSO_4^- anion, H_2SO_4 solvent).

According to the ^{1}H NMR spectra, the cation I_1^+ (formed by the expulsion of toluene) prevails. The proportion of I_1^+ exceeds 90% assuming similar extinction coefficients. The shoulder at 345 nm was ascribed to M_1^+.

When monomer ($[M]_0 = 3.5 \times 10^{-3}$ mol/L) was reacted with triflic acid ($[HO_3SCF_3]_0 = 4.9 \times 10^{-3}$ mol/L, $n = 0.71$) at −72 °C, the main peak centered at 345 nm and the sharp maxima of indan at λ = 275 and 267 nm were observed. Further addition of monomer to the reaction mixture ($[M]_0 = 2.6 \times 10^{-2}$ mol/L, $[HO_3SCF_3]_0 = 3.8 \times 10^{-3}$ mol/L, n = 6.9) resulted in a transient absorption at 480 nm and in a bathochromic shift from 345 to about 350 nm. After 3 min at −73 °C, the monomeric cation at 345 nm was reformed and then slowly disappeared ($k = 10^{-4}$ s^{-1}).

The apparent extinction coefficient of M_1^+ (λ = 345 nm), estimated from the concentration of the acid, is 12 600 ($CF_3SO_3^-$ anion) or 25 200 ($CF_3SO_3^- \cdot HO_3SCF_3$ anion).

In another experiment a large excess of monomer ($[M]_0 = 4.5 \times 10^{-3}$ mol/L, $[HO_3SCF_3]_0 = 1.8 \times 10^{-4}$ mol/L, n = 25) led to the formation of two long-lived maxima at 358 and 484 nm. Here again the initial excess of monomer seems to stabilize the active species.

2.2.3. α-Methylstyrene (MS). Cumyl chloride is more stable in solution than the p-methyl derivative. A maximum at λ = 333 nm was observed in the reaction between SbF_5 and cumyl chloride at −72 °C in CH_2Cl_2. This maximum has been attributed earlier to the monomeric cation.[7,8] The apparent extinction coefficient was equal to ϵ = 26 300.

However, in the presence of an excess of monomer at −73 °C this peak disappeared and three new maxima are formed at λ = 320, 350, and 420 nm. The maxima at λ = 320 and λ = 420 nm might be ascribed to the indanyl cations (cf. section 2.2.2). The maximum at λ = 350 nm is in the region of absorption of the cation with the p-*tert*-butyl substituent. It is possible that this maximum corresponds to a cation with an alkylated para position. However, Pepper earlier observed absorption at 350 nm by the stopped-flow method at low temperature.[28]

The reaction between monomer and acid ($[M]_0 = 4 \times 10^{-3}$ mol/L, $[HO_3SCF_3]_0 = 5 \times 10^{-3}$ mol/L, n = 0.81) in CH_2Cl_2 at −72 °C yielded species absorbing at 332 nm M_1^+ and at λ = 271 and 264 nm (indan). Assuming the extinction coefficient $\epsilon \simeq 30000$ (similar to other monomers), the yield of M_1^+ would be only 3%. A new addition of monomer ($[M]_0 = 2.5 \times 10^{-2}$ mol/L, $[HO_3SCF_3]_0 = 3.6 \times 10^{-3}$ mol/L, n = 6) led to a small increase in the yield of the monomeric cation ($\simeq$5% from the used acid), but it was still much lower than for p-alkyl-substituted monomers. Neither a bathochromic shift nor a second maximum was found.

3. Discussion

In this section we shall first discuss the ^{1}H NMR and UV results by comparing them with the literature data. We shall then briefly describe the thermodynamics of α-methylstyrene polymerization and discuss the chemistry of the elementary reactions participating in the cationic polymerization of α-methylstyrenes.

3.1. ^{1}H NMR Studies. The chemical shifts and coupling constants of the protons in M_1^+, D_I, and indanyl cations for MS, DMS, BMS, and MOMS are given in Tables I, II, and III, respectively. For the latter monomer the indanyl cation is unstable and apparently exists in equilibrium with the nonprotonated exo olefin. This is probably due to the destabilizing effect of the methoxy group in the meta position. At higher temperatures the olefin reacts with the cation to form spirobiindan (cf. eq 2).

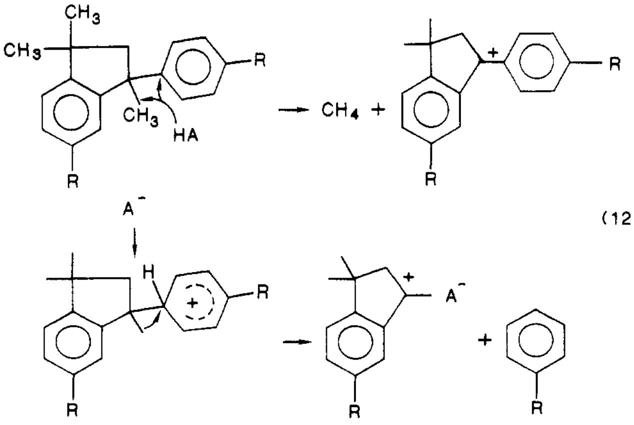
The chemical shifts of monomeric cations M_1^+ do not depend on the anion structure and coincide for $CF_3SO_3^-$ (or $CF_3SO_3^- \cdot HSO_3CF_3$) and SbF_5Cl^- counterions. The values of the chemical shifts resemble those reported for cations derived from carbinols in superacid media.[9,10] These chemical shifts have been previously correlated with the charge densities and σ^+ parameters.[11] Thus, the α-

methyl protons of the most stable cation derived from MOMS absorb at the highest field, whereas the most deshielded are protons of the least stable cation derived from MS. Indeed, this is in agreement with the yield of cations observed in protonation. DMS and BMS behave in a similar way and have similar values for the chemical shifts. The similar effects were reported for ^{13}C NMR and correlated via a new σ^{c+} scale.

For MS, DMS, and BMS only M_1^+ cations were detected in ^1H NMR spectra. For MOMS, M_2^+ and M_3^+ were found in addition to M_1^+. Dimeric and trimeric cations derived from *p*-alkyl and unsubstituted α-methylstyrenes depropagate or cyclize very rapidly to form indans, although the dimeric cation from MS was claimed to be stable at −40 °C in a superacid medium[12] which is very improbable because of the high $[HA]_0/[M]_0$ ratio. The lifetimes of M_2^+ and M_3^+ for MS, BMS, and DMS are too short even at −70 °C in CH_2Cl_2 to be observed by NMR. Cations derived from MOMS are more stable due to the *p*-methoxy group. This group makes the cation less reactive and also decreases the electron density at the carbon atom attacked in the cyclization process.[34]

The chemical shifts of the protons of the indanic dimers are shown in Table II. The methylene protons absorb giving an AB pattern ($J \approx 13$ Hz). Three methyl groups are nonequivalent due to the diamagnetic current of the aromatic nucleus. The protons in R substituents absorb at a similar field and have not been attributed to a given aromatic ring.

In Table III the chemical shifts of the indanyl cations are given. These cations were formed by the expulsion of benzene, toluene, and *tert*-butylbenzene from the corresponding indans, in the presence of triflic acid above −20 °C. The differences in chemical shifts between indanyl cations derived from MS, DMS, and BMS are much smaller than in the corresponding M_1^+ cations. The indanyl cations are stable at room temperature and slowly decompose in open systems in the presence of moisture. In general, cations formed by the expulsion of the methyl group and having two aromatic substituents should be thermodynamically more stable. However, there is no facile reaction pathway leading to 1-arylindan-1-yl cations (eq 12).



(12)

On the other hand, 1-methylindan-1-yl cations might be formed by a σ-complex and disproportionation reactions.[12] In the NMR and also in UV spectra less than 10% of 1-arylindan-1-yl cations were found. The exact mechanism of formation of these cations is not clear.

1-Methylindan-1-yl cations with *p*-methoxy substituents are not stable, and they form spirobiindan. No spirobiindan was formed for MS, DMS, and BMS.

3.2. UV Spectra. The results of our UV studies are summarized in Table IV. The maximum of absorption of dimethylphenylmethylium cation at 333 nm may be compared with the values of 326 nm for the cation derived from MS in a superacid medium,[7] with 333 nm for a cation formed in CH_2Cl_2 from cumyl chloride and $AlCl_3$,[8] and with 336 nm in the polymerization of MS by triflic acid in $C_2H_4Cl_2$ observed by a stopped-flow technique at 30 °C.[14] No UV data on para-substituted aryldimethylmethylium cations were reported in literature. The reliable extinction coefficients (BMS, MOMS) obtained in the present study are nearly 3 times higher than that found previously for MS.[7] This might be a consequence of the different reaction media and substituents. However, a lower than assumed yield of the cation in the superacid medium cannot be excluded.

In agreement with the observation made earlier for trityl cations, *p*-alkyl and *p*-methoxy substitution leads to a bathochromic shift, the latter to a larger extent.[15] Values of ϵ for trityl cations with *p*-methoxy, *p*-methyl, and *p*-*tert*-butyl groups are similar and larger than for unsubstituted salt.[15] The values of extinction coefficients for cations derived from MOMS, BMS, and MS seem to be in the vicinity of 30 000. The apparently smaller value of ϵ for DMS may have its origin in the nonquantitative formation of these cations.

Two maxima at $\lambda = 362$ nm and $\lambda = 490$ nm have already been reported in the polymerization of PMS initiated by triflic acid in CH_2Cl_2.[2] The origin of the appearance of the second maximum and the bathochromic shift of the main one ($\Delta\lambda \approx 15$ nm) are not completely clear. There are two possible explanations for the formation of two maxima at higher initial monomer concentration. The first one is to ascribe the new spectrum to the complexes between carbenium ions and olefins (i.e. monomer or linear oligomers) and the second one to polymeric cations. These cations might interact strongly with the adjacent aromatic nuclei; this interaction has also been named as space polarization.[16] In fact, UV spectra for the cationic dimerization of 1,1-diphenylethylene have already been interpreted by the participation of both systems discussed above.[17]

The interactions between aromatics and electron acceptors leading to the formation of charge-transfer complexes are very well-known. First they were quantitatively determined for an I_2 complex.[18] In the presence of aromatic compounds, the absorption of I_2 shifted from 512 nm to shorter wavelengths by not more than 20 nm and a second maximum appeared in the range of 300–370 nm.[19] As discussed later by Mulliken[20,21] "the iodine molecule is present in its aromatic complexes without more than a small change in its electronic structure", the second transition being attributed to the complex as a whole. Later Winstein[22] has postulated similar complexes for the tropylium cation and more recently Heublein for the trityl cation.[23] The values of the equilibrium constants K were however low. Values of the order of 4 L/mol were calculated for Ph_3C^+–styrene.[23] K values below 1 L/mol were found for benzene–I_2 or benzene–Ph_3C^+ complexes. With hexamethylbenzene larger values were determined (K = 68 L/mol with Ph_3C^+, $FeCl_4^-$ in CH_2Cl_2 at 0 °C). The complexations were only slightly exothermic ($-\Delta H \leqslant 4$ kcal·mol^{-1}). Thus, the effect of temperature cannot be significant.

In these studies with DMS, BMS, and MOMS we have found that even at very low monomer concentration ($[M] < 10^{-3}$ mol/L) two maxima are present. This should suggest a very large value of the equilibrium constant ($K \geqslant 10^3$ L/mol), much larger than those observed for trityl cations and styrenes.

On the other hand many chemical reactions occur much more rapidly intramolecularly than intermolecularly. The so-called effective molarity, being the ratio of the rate constants of intra- and intermolecular reactions may be as large as $[M]_{eff} \approx 10^5$–10^6 mol/L.[24] This means that a properly located neighboring group may increase the complexation to a much higher extent than predicted from the studies of bimolecular reactions.

As shown in the previous paper,[1] for MOMS the nonisomerized cations (M_1^+, M_2^+, and probably M_n^+) have only one absorption maximum at 368 nm. The bathochromic shift of this maximum (to 382 nm) and the appearance of the second maximum at 460 nm were observed for the isomerized cation M_{3i}^+ in which cation is complexed by two adjacent aromatic rings.

Thus, at present we are inclined to believe that the bathochromic shift of the main maximum and formation of the second one correspond to the internal complexation of the carbenium ion, but the stabilization of carbenium ions observed at higher initial monomer concentration suggests additional contribution of the external complexation of the ions by the monomer and/or linear oligomers.

3.3. Thermodynamics of Polymerization of α-Methylstyrenes. In contrast to unsubstituted styrenes, the high monomer equilibrium concentration in the polymerization of α-methylstyrenes is a well-known phenomenon.

The values of the monomer equilibrium concentrations of MS, PMS, and BMS at different temperatures are known[25-27] (e.g., $[M]_e \approx 10^{-2}$ mol/L at -60 °C). These values were determined for anionic polymerizations in THF. The thermodynamics of polymerization is independent of mechanism and similar values of $[M]_e$ should be obtained in anionic, cationic, or radical processes, provided that a high polymer of the same structure is formed and the solvent is the same.

Usually the equilibrium constants for reactions involving high polymers are quite different from those involving oligomers. Therefore, low molecular weight oligomers might be formed even below $[M]_e$. The equilibrium constant of the reaction modelling the dimerization process (the monomeric anion is not stable) is $K_2 = 750$ L/mol at 0 °C.[29] On the other hand, the equilibrium constant in the polymerization is $K_\infty = 1.35$ L/mol at 0 °C ($K_\infty^{-1} = [M]_e = 0.76$ mol/L). Dimers may be formed even at a monomer concentration as low as $[M] \approx 0.002$ mol/L ($> K_2^{-1}$). Of course, a possible mechanism of transformation of living growing oligomers into olefin-terminated oligomers is necessary.

In cationic polymerization, transfer reactions occur very easily, giving linear dimers and trimers. Recently, in the polymerization of PMS initiated by triflic acid at low initial monomer concentration ($[M]_0 < 0.03$ mol/L), only linear dimers and trimers were formed at -56 °C.[2] However, at $[M]_0 = 0.11$ mol/L, about 35% of polymer ($DP_n \simeq 20$) was formed.

Thus, at concentrations of monomer below $[M]_e$, linear oligomers are easily formed in cationic polymerization. In some systems the polymer is not formed even if $[M]_0 > [M]_e$. This is the case of experiments with relatively high concentration of acid. However, even at lower $[HA]_0$ the oligomers may be formed at the cost of polymer. In the polymerization of MS, DMS, and PMS the final product is the irreversibly formed indan.

3.4. Elementary Reactions. The cationic polymerization of α-methylstyrenes consists of several elementary reactions. Carbenium ions are generated by reversible protonation (A). It is possible that the dimeric form of the acid is the active one (B) and the anion is associated with one (or more) molecule of the acid. M_1^+ reacts reversibly with the monomer to form M_2^+ (C), and this later gives M_3^+ (D) etc. The equilibrium constants for the formation of M_2^+ and M_3^+ are much higher than the equilibrium constant of polymerization (E). Transfer reactions proceed either with the monomer (F) or with the counterion (G). Active species alkylate aromatic rings (H). The most probable reaction of this type is the intramolecular formation of indan M_n^I. At higher relative concentrations, the monomer may successfully compete with the anion for the acid (I). The monomer or other olefins may also form complexes with carbenium ions (J). Growing active centers may react not only with a monomer but also with olefins. Reaction with the exo dimer will give an isomerized trimeric cation M_{3i}^+, observed and identified for MOMS (K). The isomerized species may also be formed by the intramolecular 1,3-methide shift (L). These reactions are shown in Scheme I which has been constructed employing the results from the cationic polymerization of MOMS[1] and supplemented with the results for other α-methylstyrenes discussed in this paper.

Scheme I

$$(HA)_2 + M \rightleftharpoons M_1^+,(HA)_2^- \qquad (A)$$

$$2HA \rightleftharpoons (HA)_2 \qquad (B)$$

$$M_1^+,HA_2^- + M \rightleftharpoons M_2^+,HA_2^- \qquad (C)$$

$$M_2^+,HA_2^- + M \rightleftharpoons M_3^+,HA_2^- \qquad (D)$$

$$M_n^+,HA_2^- + M \rightleftharpoons M_{n+1}^+,HA_2^- \qquad (E)$$

$$M_n^+,HA_2^- + M \rightleftharpoons M_n^= + M_1^+,HA_2^- \qquad (F)$$

$$M_n^+,HA_2^- \rightleftharpoons M_n^= + (HA)_2 \qquad (G)$$

$$M_n^+,HA_2^- \rightleftharpoons M_n^I + (HA)_2 \qquad (H)$$

$$M_n^+,HA_2^- + M \rightleftharpoons M_n^+,A^- + M_1^+,A^- \qquad (I)$$

$$M_n^+,HA_2^- + M \rightleftharpoons M_n^+,M,HA_2^- \qquad (J)$$

$$M_n^+,HA_2^- + M_m^= \rightleftharpoons M_{(n+m)_i}{}^+HA_2^- \qquad (K)$$

$$M_n^+,HA_2^- \rightleftharpoons M_{ni}^+,HA_2^- \qquad (L)$$

All the carbenium ions pairs are in equilibrium with the unpaired ions (we avoid the expression free ions because carbenium ions are generally associated with monomer, solvent, or polymer). Covalent esters were never observed by NMR. For the sake of simplicity we wrote the elementary reactions for ion pairs with the HA_2^- counterion.

Monomeric cations were also generated from the corresponding chlorides and SbF_5 (cf. eq 3). The complex anion SbF_5Cl^- does not abstract protons; thus deprotonation is absent. The interactions between cumyl chlorides and SbF_5 are very exothermic. In CH_2Cl_2 the enthalpy of this reaction equals $\Delta H° = -19$ kcal/mol.[30] With the assumption of the typical entropy change in a 2:1 reaction, $\Delta S° \simeq -34$ cal/(mol·K) (accounting for the loss of three degrees of translational freedom), the values of the equilibrium constants $K = 10^6$ L/mol at room temperature and $K = 10^{13}$ L/mol at -70 °C can be calculated. Thus, even at room temperature and at relatively high dilution ($[C]_0 \simeq 10^{-4}$ mol/L), more than 90% of the chloride is ionized. At lower temperature and higher concentration the formation of ions is quantitative.

Let us now briefly discuss the reactions described in Scheme I.

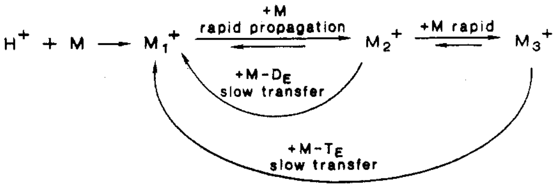
(A) and (B). Several indirect observations indicating the autoassociations of strong protonic acids were made. However, neither the kinetic nor thermodynamic parameters of this association have been determined. The structure of the anion in the case of triflic acid was deduced to be HA_2^- in the oligomerization of 3-phenylindene and $H_2A_3^-$ in the oligomerization of 1,1-diphenylethylene.[4] The structure of anion may depend on the basicity of the monomer and on the ratio [M]/[HA]. However, for 1,1-DPE, the degree of association seemed to be practically independent of the [M]/[HA] ratio. For MOMS, the anion appears to be HA_2^- at [M]/[HA] < 3. The continuous shift from HA_2^- to the A^- structure with an increase of the above ratio can be deduced from the increase of the absorption at 382 nm in UV spectra. For BMS and DMS the anion probably also has the structure HA_2^-.

Reactions between triflic acid and monomers generate M_1^+. This reaction seems to be very fast. At 30 °C in $C_2H_4Cl_2$, with the assumption of a simple bimolecular reaction between MS and CF_3SO_3H, the rate constants of protonation k_i were calculated to be about 10^3 mol^{-1}·L·s^{-1}.[14] At −30 °C in CH_2Cl_2, the formation of carbenium ions was completed before 0.02 s for the PMS–CF_3SO_3H system. Thus, the value of k_i would be at least 10^3 mol^{-1}·L·s^{-1} assuming bimolecular reaction. The rate constant k_{-i} of the reverse reaction, deprotonation, may be estimated from the rate of decomposition of M_1^+ (see eq 8). At −60 °C for MS, DMS, and BMS this rate constant k_{-i} is about 10^{-4} s^{-1}. For MOMS, $k_{-i} < 10^{-7}$ s^{-1}. Both values indicate high equilibrium constants for protonation.

(C)–(E) Inspection of molecular models shows that addition of M to M_1^+ might be more favored due to a lower steric hindrance than in reactions with M_2^+, M_3^+, or M_n^+. The values of the propagation rate constants for MS in $C_2H_4Cl_2$ were claimed to be $k_p = 3 \times 10^4$ mol^{-1}·L·s^{-1} with triflic acid and $k_p > 10^6$ mol^{-1}·L·s^{-1} with sulfuric acid at 30 °C.[14] However, the experimental conditions ($[M]_0 \ll [M]_e$) did not permit the formation of the polymer. The structure of the products was not reported. It is possible that the measured rate of monomer consumption was not related to propagation but to the transfer reaction (cf. later discussion for PMS). Usually reactivities of ions and ion pairs in cationic polymerization are similar and do not depend on anion structure. The higher k_p for H_2SO_4 may be attributed to a more rapid transfer with this acid.

The depropagation rate constant for the polymer chain can be calculated from the equation $k_d = k_p[M]_e$. However, depropagation from M_2^+ and M_3^+ is considerably slower.

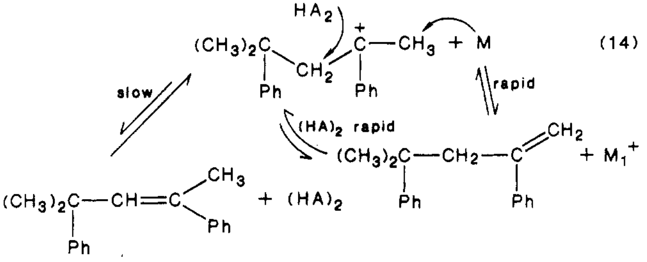
(F) In a recent study of cationic polymerization of PMS with CF_3SO_3H,[2] the rate constant of bimolecular consumption of monomer at −40 °C, k_M, could be estimated to be about 10^4 mol^{-1}·L·s^{-1} when $[M] < [M]_e$. According to the authors of this study, "the propagation rate observed at higher [M] is larger and deviates significantly from linearity." It is possible that at higher [M], propagation is possible (polymer with $DP_n \simeq 20$ is formed in 35% yield), whereas at $[M] < [M]_e$ the rate-limiting step is a bimolecular transfer to monomer (eq 13).



(13)

A similar slow transfer to monomer may occur with M_3^+. If in this system all other side reactions were absent, the observed degree of polymerization ($DP_n \simeq 20$) might correspond to the ratio k_p/k_{tr}. For a k_{tr} equal to 10^4 mol^{-1}·L·s^{-1}, the k_p value should be 2×10^5 mol^{-1}·L·s^{-1}. The rate constant of monomer consumption for PMS at −40 °C ($k_M \simeq 10^4$ mol^{-1}·L·s^{-1}) is very close to the one found for MS at 30 °C ($k_M \simeq 3 \times 10^4$ mol^{-1}·L·s^{-1}).[14] A small energy of activation was found for PMS ($E_e \simeq 2$ kcal/mol).

(G) In the oligomerization of PMS at −40 °C, exo olefins were formed (^{1}H NMR absorptions at 5.03 and 4.69 ppm). In the oligomerization of MOMS at relatively higher $[M]_0$, the exo dimer first formed can be converted into the endo dimer at longer reaction times.[1] At low $[M]_0$, only the endo dimer was observed. The endo dimer may be the thermodynamic product and could be formed through a relatively slower transfer to the counterion. The much more rapid transfer to monomer would yield the kinetic product, i.e. the exo dimer. This product may be reversibly protonated and isomerized to the endo dimer (eq 14).



(14)

The methylene protons may be more difficult to approach for the monomer molecule than for the counterion.

(H) Another type of transfer reaction results in indan formation. The molecule of acid capable of reinitiation is released, but a "dead" macromolecule is obtained. The reaction is relatively slow at −70 °C ($k_I \simeq 10^{-2}$ s^{-1} in the absence of excess monomer for BMS) but has a higher activation energy than the other participating reactions. For MOMS at −70 °C, $k_I < 10^{-7}$ s^{-1} but at 0 °C $k_I \approx 10^{-3}$ s^{-1}. Monomer and dimers of α-methylstyrenes are converted quantitatively into indans in the presence of acid if $[M] < [M]_e$. The rate of this conversion depends on [HA] and time. The reaction can be stopped before indan is formed, yielding olefin-terminated oligomers.

The rate of indan formation compared to α-methylstyrenes is reduced for the more stable *p*-alkyl-substituted cations. However, only the *p*-methoxy group prevents the formation of indan below −40 °C. This group not only better stabilizes cations ($\sigma^+ = -0.78$) but also reduces the charge density on the orthocarbon atom in the second ring ($\sigma_m = +0.12$). For *p*-methyl group $\sigma^+ = -0.31$ and $\sigma_m = -0.007$.[31]

(J) The presence of an excess olefin reduces the rate of indan formation and stabilizes the cations. These interactions may lead to the formation of complexes between monomer (or linear oligomers) and carbenium ions. Qualitative observations suggest a strong complexation. Recent results in the polymerization of *p*-methoxystyrene might indicate that the lifetime of such a complex exceeds a few seconds, i.e. time necessary to build an entire macromolecule.[32] It seems that the olefin involved in this complex is not capable of propagation, which means that complexation is not a preliminary coordination before monomer addition. The energy of the molecule of monomer participating in the complex is so much reduced that it cannot be incorporated. Only a newly approaching monomer molecule may have energy high enough to react with the carbenium ion in the propagation step.

(K) Exo olefins have reactivities similar to monomer. They can react with the growing carbenium ion forming isomerized cations in the way similar to the reaction of M_1^+ with D_{exo} discussed for MOMS.[1] These cations have different absorption patterns in UV due to the interactions with two neighboring aromatic nuclei.

(L) The isomerized cations may also be formed via 1,3-methide shift in the intramolecular reaction. 1,3-Hydride shift proceeds with low activation energy $E = 8$

kcal/mol.[35,36] 1,3-Shifts for the larger substituents in acyclic systems were not yet observed, presumably due to steric effects. The immediate formation of the second maximum observed in oligomerization of PMS[2] may suggest the rapid intramolecular shift (or external complexation).

Thus, the overall polymerization process can be described in the following way: monomeric cations formed in the reaction with the acid are rapidly converted into M_2^+ (and M_3^+) in the presence of monomer. If $[M] < [M]_e$, growing carbenium cations may no longer be formed. Carbenium ions and monomer may lead to propagation, complexation, and formation of exo olefin-terminated oligomers. The exo linear dimer plus M_1^+ gives M_{3i}^+. These cations might also be formed intramolecularly. The exo oligomers are reversibly protonated by the acid. The carbenium ions formed may lose protons by spontaneous transfer with counterions, yielding thermodynamically more stable endo olefins.

Later indan is formed. The rate of indan formation is reduced by para substitution and for the *p*-methoxy group indan is not formed below −40 °C. At room temperature indan, in the presence of acid, gives indanylium cations for MS, DMS, and BMS and spirobiindan for MOMS.

4. Experimental Section

Materials. Monomers. DMS and BMS were prepared from commercially available *p*-methyl- and *p-tert*-butylacetophenones by reaction with methylmagnesium bromide in diethyl ether solutions. The formed carbinols were dehydrated (with I_2) to olefins directly in a spinning band column Perkin-Elmer 251: DMS, bp 69 °C (10 mmHg); BMS, bp 115 °C (10 mmHg).[33] All monomers were dried on Na mirrors and stored at −20 °C under vacuum.

Chlorides. All cumyl chlorides were prepared by bubbling dry HCl through CH_2Cl_2 solutions of carbinols following Brown's procedure.[34] The dried chlorides were distilled: MS–Cl, bp 56 °C (1.5 mmHg); DMS–Cl, bp 42 °C (10^{-3} mmHg). BMS–Cl was crystallized from CH_2Cl_2/hexane. The chlorides were stored at −20 °C.

Solvents. Both CD_2Cl_2 and CH_2Cl_2 were first treated with oleum for 10 h, then neutralized, washed with H_2O, dried with $CaCl_2$, distilled, and dried twice on P_2O_5 films and four times on Na mirrors. Triflic acid and SbF_5 were distilled four times under vacuum in an all glass system and eventually into capillaries of known diameters equipped with breakseals.

Solutions of SbF_5, acid, and monomers were prepared under vacuum and distributed into calibrated cylinders equipped with breakseals.

Procedures. ^{1}H NMR spectra were recorded by using a 250-MHz Brücker instrument. UV spectra were recorded by using a Cary 118 spectrometer. All solutions were prepared under vacuum as described previously.[1]

Solutions of chlorides were prepared fewer than 2 min before reaction with SbF_5 by breaking the ampule containing the pure chloride (solid for BMS–Cl) in CH_2Cl_2 and introducing it immediately (through a breakseal) into the SbF_5 solution.

Registry No. BMS, 25163-88-6; DMS, 1195-32-0; MS, 98-83-9; $C_6H_5C(CH_3)_2^+$, 16804-70-9; 4-$H_3CC_6H_4C(CH_3)_2^+$, 20605-66-7; 4-$(CH_3)_3CC_6H_4C(CH_3)_2^+$, 90763-71-6; 4-$C_3COC_6H_4C(CH_3)_2^+$, 22666-71-3; 1,1,3-trimethyl-3-phenylindan, 3910-35-8; 1,1,3-tetramethyl-3-(4-methylphenyl)indan, 1153-36-2; 1,1,3-trimethyl-5-*tert*-butyl-3-(4-*tert*-butylphenyl)indan, 110528-60-4; 1,1,3-trimethyl-5-methoxy-3-(4-methoxyphenyl)indan, 108122-20-9; 1,1,3-trimethylindanyl cation, 110528-61-5; 1,1,3,5-tetramethylindanyl cation, 110528-62-6; 1,1,3-trimethyl-5-*tert*-butylindanyl cation, 110528-63-7.

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