

Stable Carbocationic Species Observed During the Oligomerization of *p*-Isopropyl- α -Methylstyrene Initiated by $\text{CF}_3\text{SO}_3\text{H}$ in CH_2Cl_2 Solution

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Summary

The cationic oligomerization of *p*-isopropyl- α -methylstyrene by $\text{CF}_3\text{SO}_3\text{H}$ in dichloromethane has been investigated. The electronic spectrum of the corresponding active species showed two absorption maxima at 362 and 490 nm. The reaction did not give high polymers but rather dimers and trimers as major products, the proportion of olefinic dimers and trimers increasing at lower temperatures compared with the indanic products. Oligomers with $\text{DP}_n \approx 20$ were obtained at -58°C for a monomer to initiator ratio greater than 1800.

Introduction

A major problem in cationic polymerization remains the determination of the nature and concentration of propagating species. This is particularly true in the case of protonic acid initiation. Since the work of Plesch (1,2), Higashimura (3) and Pepper (4) and the early controversy about "pseudocationic" polymerization, many studies have been made on ethylenic monomers-superacid systems. Stopped-flow polymerization experiments have been reported on styrene (5,6), *p*-methoxystyrene (7,8,9,10) and α -methylstyrene (11) where strong acid initiators (HClO_4 or $\text{CF}_3\text{SO}_3\text{H}$) were used. The interpretation was based upon the appearance of an absorbing species usually having a single UV peak (340 nm for styrene, 380 nm for *p*-methoxystyrene, 334 nm for α -methyl styrene). These ionic species were considered as the propagating ones even if no direct proof was afforded.

These results led us to investigate a system in which significantly more stable propagating species might be obtained. We report here preliminary results concerning the oligomerization of *p*-isopropyl- α -methylstyrene initiated by $\text{CF}_3\text{SO}_3\text{H}$ in CH_2Cl_2 solution.

Experimental

The commercial monomer (Aldrich) was carefully distilled on a spinning band column until chromatographically pure. It was further purified, dried and stored under high vacuum in sealed vessels according to procedures described previously, as was the dichloromethane (12).

The commercial triflic acid (Merck) was purified (by distillation in sealed vessels), diluted with CH_2Cl_2 and distributed in 4 ml breakable phials under high vacuum. The calculated amount of $\text{CF}_3\text{SO}_3\text{H}$ introduced into each phial was 1.13×10^{-5} mole, i.e. less than 1 μl , except in experiments G where it was half that amount and H where it was three times greater.

Such low concentrations could not be measured by NMR. We can thus only give an upper limit for the concentration because of the well-known adsorption of triflic acid on glassware which reduces the actual concentration in the experiment. Thus the effective concentration of triflic acid is reduced, but by no more than 25%.

Polymerizations were carried out in a completely sealed adiabatic calorimeter developed in this laboratory (13). The UV-visible spectrum, as well as the temperature rise of the polymerizing mixture, were recorded simultaneously.

GPC of the products were performed on μ -styragel columns with THF as eluent.

Results and discussion.

The polymerization of p-isopropyl- α -methylstyrene by $\text{CF}_3\text{SO}_3\text{H}$ has been studied in dichloromethane at various monomer and initiator concentrations between -58°C and -20°C . The experiments are summarized in Table 1. All the reactions were followed for 5 minutes before terminating with CH_3OH .

In the temperature range -58°C to -20°C , two absorption bands appear instantaneously in the visible spectrum (362 nm and 490 nm) upon mixing the monomer and the initiator (fig. 1). At -58°C the intensity of the two bands remained perfectly stable throughout the experiment. However at -20°C these two bands disappear rapidly after about 1 minute, and at

Table 1. Oligomerization of p-isopropyl- α -methylstyrene by $\text{CF}_3\text{SO}_3\text{H}$ in CH_2Cl_2 solution at various temperatures.

Exp.	T ^o C	Monomer $\frac{ \text{M} _{\text{e}_1}}{\text{M.l}^2 \times 10^2}$	$\text{CF}_3\text{SO}_3\text{H}$ $\frac{ \text{A} _{\text{e}_1}}{\text{M.l}^4 \times 10^4}$	$\frac{ \text{M} _{\text{o}}}{ \text{A} _{\text{o}}}$ ratio	R _p max. $1.\text{M}^{-1}.\text{s}^{-1}$	O.D at 362nm 1=.625cm	monomer conver- sion %	G P C analysis
A	-58	1.17	1	120	4.25	1.046	100	$\text{M}_4 + \text{M}_3 + \text{M}_2$
B	-58	2.78	1	280	8.38	0.968	100	oligom. + $\text{M}_4 + \text{M}_3 + \text{M}_2$
C	-56	11.30	0.63	1800	37.46	0.570	98	$\overline{\text{DP}}_{\text{n}} \approx 19$ + oligom. + $\text{M}_4 + \text{M}_3 + \text{M}_2$
D	-40	2.74	1	275	8.03	0.906	-	$\text{M}_3 + \text{M}_2$
E	-30	2.68	0.63	425	8.98	0.634	100	$\text{M}_3 + \text{M}_2$
F	-20	2.40	0.80	300	10.80	0.764	77	$\text{M}_3 + \text{M}_2$
G	-40	2.80	0.35	800	3.07	0.342	100	$\text{M}_3 + \text{M}_2$
H	-40	2.46	1.40	175	9.77	1.382	100	$\text{M}_3 + \text{M}_2$

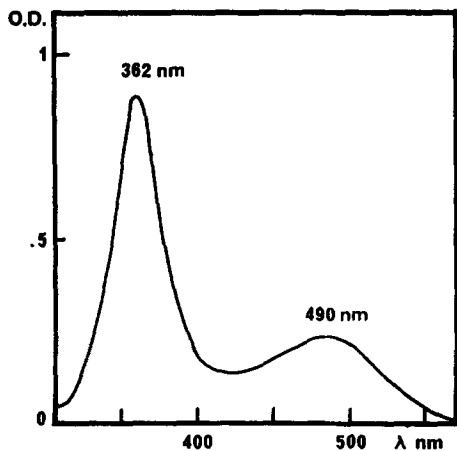


Figure 1:

Visible absorption spectrum
at $t = 3$ min. in experiment B
 $[M]_0 = 2.78 \times 10^{-2} \text{ M.l}^{-1}$
 $[A]_0 = 1 \times 10^{-4} \text{ M.l}^{-1}$
at -58°C in CH_2Cl_2 .

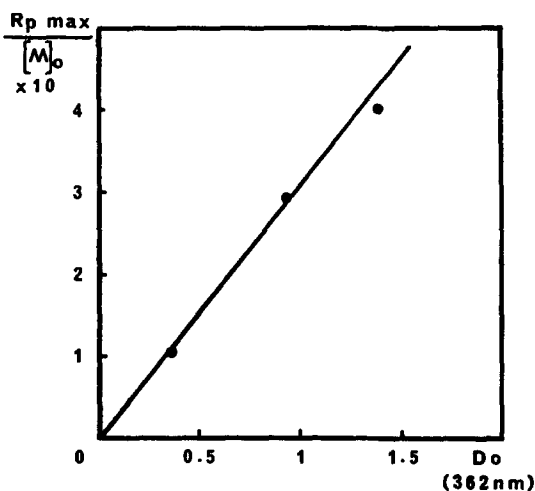


Figure 2:

Proportionality between rate of
oligomerization and optical
density at 362 nm in exp. D,G,H
 $[M]_0 = 2.5 \text{ to } 2.8 \times 10^{-2} \text{ M.l}^{-1}$
at -40°C .

ambient temperature, they disappear after 6 seconds.

In order to investigate the nature of the species absorbing at 362 nm which could be the propagating cation, we followed the reaction at different initiator concentrations at -40°C with similar monomer concentrations in the three experiments D, G and H. The observed optical densities at 362 nm are reported in Table 1. In the absence of an extinction coefficient (ϵ) value for the absorbing species, we plotted the rate of the reaction (R_{max}) as a function of the plateau value of optical density at 362 nm (D_0)^p which is reasonably assumed to be proportional to the concentration of this species. Fig. 2 shows that there is a linear relationship between D_0 and R_{max} which shows that the absorbing and the propagating species are closely related and perhaps the same.

We must point out however that λ_{max} values reported by several authors for the related α -methylstyryl cation are very different: respectively 326 nm for α -methylstyrene in superacid medium (14), 327 nm

for the cation derived from isopropyl-benzylacetate in H_2SO_4 (15), 333 nm for the α -methylstyryl cation derived from the reaction of the corresponding chloride with $AlCl_3$ in CH_2Cl_2 solution (16), and 336 nm as determined from rapid scan spectra of the polymerization of α -methylstyrene by triflic acid in dichloroethane (11). Such a small shift in the λ_{max} is generally observed when changing from a superacid medium to a chlorinated solvent and the different λ_{max} thus correspond to the same species. These data do not support the hypothesis that the species we observe at 362 nm is the propagating p-isopropyl- α -methylstyryl cation.

On the other hand, the λ_{max} reported by Dorfman for the free benzylic cation is 362 nm, and is identical to that of the corresponding free anion (17,18). The λ_{max} of the ion pair p-isopropyl- α -methylstyryl / Na^+ in THF is 347 nm (19), which is 15 nm lower than the λ_{max} that we observed for the supposed corresponding cation. Such a shift in the maximum wavelength of the active species arising from counterion effects has however been observed previously (for the fluorenyl ion (20)) and our assumption could thus be considered as not unreasonable.

The intensity of the 490 nm peak is about 30% of the optical density at 362 nm, and much larger than the corresponding high wavelength band observed around 400 nm in the α -methylstyryl cation spectrum (corresponding to less than 10% of the optical density at 326 nm). This 490 nm band might arise from a distinct species, possibly a trienyl or a tetraenyl cation.

From these experiments and from preliminary measurements with a low temperature high vacuum prototype stopped-flow apparatus we could also conclude that the initiation was complete and extremely rapid with respect to propagation. These stopped-flow measurements showed that the absorbing species appear 10 to 20 msec after mixing the monomer and the initiator at temperatures between $-40^\circ C$ and $-20^\circ C$, that is before significant propagation takes place. The initiation process thus appears to be instantaneous with respect to propagation time (c.a. 5 sec. for the experiments reported in Table 1.). Owing to technical problems these stopped-flow experiments did not give quantitative kinetic results.

The fact that the initiation was complete was derived from semi-quantitative estimations of the ϵ at 362 nm from the spectro-calorimetric experiments. Initiation studies with triflic acid have shown that up to three molecules may be necessary to initiate the propagating chain (21,22). Assuming that the initiation is complete and would require either 1, 2 or 3 triflic acid molecules to initiate each kinetic chain, we could determine minimum ϵ values for the active species from the optical densities observed at 362 nm when different CF_3SO_3H concentrations were used. These ϵ values are minimum values because as we pointed out in the experimental, the actual amount of triflic acid introduced in the reactor is less than the value calculated from the dilution of the initiator solutions, which leads to underestimated values for the extinction coefficient. At $-58^\circ C$, we obtained $\epsilon = 16000 \text{ l.mole}^{-1} \text{ .cm}^{-1}$ if one CF_3SO_3H molecule gives one cation and obviously 32000 if two CF_3SO_3H are necessary and 48000 for three.

If the initiation was not complete and if a few per cent of the triflic acid were necessary to initiate the reaction as is the case for styrene (5), the same calculation would lead to ϵ values over one million which is highly unlikely for such a cation. Moreover considering the $\epsilon = 15000 \text{ l.mole}^{-1} \text{ .cm}^{-1}$ determined at 327 nm in H_2SO_4 medium for the α -methylstyryl cation (15), it might be concluded that only one (or two at most) molecule of triflic acid is necessary to produce one cation.

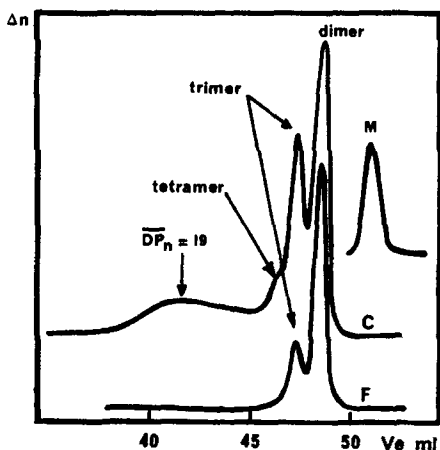


Figure 3:

Gel permeation chromatograms
of products from experiment C:
 $T = -56^{\circ}\text{C}$, $|M|_0/|A|_0 \approx 1800$,
and experiment F:
 $T = -20^{\circ}\text{C}$, $|M|_0/|A|_0 \approx 300$

GPC analysis of the products showed that high polymers were not obtained in these reactions, but only dimers and trimers at temperatures of -40°C and above (fig. 3.).

^1H NMR spectra of the dimers and trimers showed that in the very low temperature experiments, over 90% of olefinic terminated products were present with the characteristic AB signal at 5.03 and 4.69 ppm, whereas at -20°C the termination yielded almost exclusively cyclic compounds with signals between 2.03 and 2.43 ppm (23). A small proportion of olefinic products could be observed at intermediate temperatures.

At -58°C , when the ratio of monomer to initiator was greater than 1500, we observed the formation of a significant proportion of oligomers with higher \overline{DP}_n values (≈ 20) as shown in fig. 3.

The proportion and \overline{DP}_n of oligomers decreased with decreasing values of $|M|_0/|A|_0$ and of temperature; only dimers to tetramers were obtained when $|M|_0/|A|_0 \approx 300$ or less.

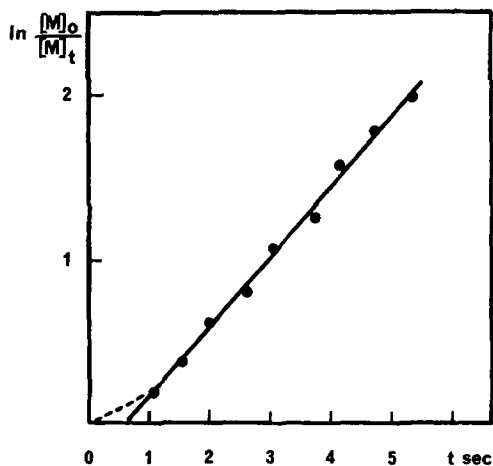


Figure 4:

Internally determined order
with respect to monomer

$$\text{Exp. D: } |M|_0 = 2.74 \times 10^{-2} \text{ M.l}^{-1}$$

$$|A|_0 = 1 \times 10^{-4} \text{ M.l}^{-1}$$

$$T = -40^{\circ}\text{C}$$

Between -60°C and -20°C the mean enthalpy determined for this reaction was $\Delta H = -7.5 \pm 0.4$ kcal/mole.

The activation energy for the reaction was determined from the Arrhenius plot of the maximum rate of reaction (R_{max}) versus $1/T$ and gave a low positive value of about 2 kcal/mole.

The internal order with respect to monomer is unity (fig. 4). When externally determined, from a (R/D_0) versus $|M|_0$ plot, only the values corresponding to the lower initial monomer concentration fitted with a first order rate. The propagation rate observed at higher monomer concentration is larger and deviates significantly from linearity. We have no explanation yet for this last result which is under investigation.

Conclusion

In the $\text{CF}_3\text{SO}_3\text{H}$ -p-isopropyl- α -methylstyrene system, below -30°C , a very high proportion of the initiator is consumed in the first 10 msec of the reaction and leads to the formation of stable ionic species. This is noticeably different from Pepper's observation with styrene that only about 1% of the initiator was consumed leading to ionic species which were not stable even at -80°C .

In spite of a higher λ_{max} , the order of magnitude of the ϵ we calculated for the ionic species we observe is in agreement with those reported previously for the α -methylstyryl cation, assuming that one triflic acid molecule is necessary to produce one cation. The stability of this species during the whole reaction supports the hypothesis that it could be an active carbocation. This interpretation is further supported by the proportionality between the rate of oligomerization and the optical density at 362 nm.

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