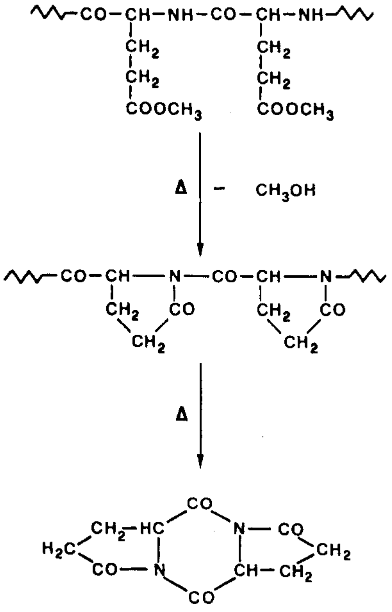
Comments on the Paper "Thermal Decomposition of Poly(γ-methyl L-glutamate)"

A paper dealing with the pyrolysis-gas chromatography-mass spectrometry (GC-MS) of poly(γ-methyl L-glutamate) (PMLG) appeared recently in this journal.[1] Pyrolysis products of up to m/z 85 were eluted from the GC column and identified by MS.

On the basis of these results, it was concluded that the primary decomposition products evolving from PMLG are methanol, carbon dioxide, methane, and some other gaseous materials.[1]

Scheme I

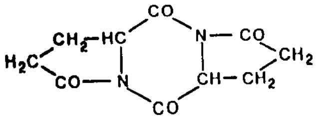


I

The authors were, apparently, unaware of our recent results[2] on the thermal decomposition of PMLG, investigated by direct pyrolysis-mass spectrometry (DP-MS).

In the DP-MS technique,[2] polymers are introduced via a direct insertion probe and the temperature is increased gradually to a point at which thermal decomposition reactions occur; the volatile products formed are then ionized and detected.

Two diketopiperazines (I and II) were detected, together with methanol, among the pyrolysis products of PMLG.[2]



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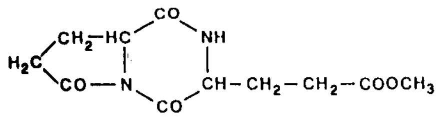

II

These findings gave us a firm basis so as to propose[2] a primary thermal fragmentation mechanism for PMLG (Scheme I).

In fact, one of the advantages of the DP-MS technique is that the pyrolysis is accomplished under a high vacuum and, therefore, that the thermal products formed are volatilized and removed readily from the hot zone. This, together with the low probability of molecular collision and the fast detection, reduces, to a large extent, the occurrence of secondary reactions. Consequently, the thermal fragments detected are due almost exclusively to primary reactions. The information thus obtained is, therefore, of particular importance in order to assess the primary thermal decomposition mechanism of a particular polymer.[2]

Secondary and/or tertiary decomposition reactions cannot be avoided by using pyrolysis-GC-MS, since the pyrolysis is performed at atmospheric pressure and the pyrolysis products are kept for some time in the GC column at a high temperature.

In view of our previous DP-MS results,[2] the pyrolysis products of PMLG which were detected by pyrolysis-GC-MS in ref 1 appear to be smaller, secondary, products. It is difficult to derive a mechanism of primary thermal decomposition of PMLG from this kind of information (see Scheme I).

Rather, it should be realized that pyrolysis-GC-MS experiments are actually concerned with the thermal decomposition of diketopiperazines I and II, which are, themselves, the primary pyrolysis products originating from PMLG.

Acknowledgment. Partial financial support from the Italian Ministry of Public Education and from Consiglio Nazionale delle Ricerche (Roma) is gratefully acknowledged.

Registry No. I, 14612-22-7; II, 104807-55-8; PMLG (homopolymer), 25086-16-2; PMLG (SRU), 25036-43-5.

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Received May 28, 1986

Trialkylsilyl Triflates, Novel Initiators for Cationic Polymerization

We wish to report that trialkylsilyl trifluoromethanesulfonates are highly effective novel initiators for the cationic polymerization of vinyl monomers and oxacyclic compounds.

Trialkylsilyl trifluoromethanesulfonates (triflates) have enjoyed wide use as electrophilic reagents in organic chemistry.[1-5] They are highly reactive toward electron-rich olefins and to carbonyl and oxacyclic compounds. Nevertheless recent authoritative reviews[6-10] contain no mention of their use as initiators for the cationic polymerization of such monomers.

Representative results for the initiation of the cationic polymerization of some common electron-rich monomers, using trimethylsilyl triflate (**1**) and triisopropylsilyl triflate (**2**), are given in Table I. Careful purification of reagents ensured that triflic acid was not responsible for these polymerizations. The polymerizations proceed rapidly at

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Table I
Polymerization of Electron-Rich Vinyl and Cyclic Monomers by Trialkylsilyl Triflates

monomer	concn,[a] mol·L^{-1}	initiator	mol %	temp, °C	time, h	yield, %	MW[b]	MWD[c]	η_{inh}[d]
N-vinylcarbazole	0.3	**1**	1.0	−78	1 min	84	80 000	3.77	0.21
p-methoxystyrene	1.0	**1**	1.0	−78	10 min	100	390 000	1.72	0.96
	1.0	**2**	1.0	−78	10 min	18	180 000	3.49	0.52
isobutyl vinyl ether	1.0	**1**	1.0	−78	24	100	3 000		0.28
α-methylstyrene	1.0	**1**	1.0	−78	24	91	22 000	1.98	0.12
	1.0	**2**	1.0	−78	24	90	8 600	2.12	0.10
styrene	1.0	**1**	1.0	−78	24	82	140 000		0.51
trioxane	bulk	**1**	1.0	65	4	100			
cyclohexene oxide	bulk	**1**	3.0	28	24	83	1 900		0.09
1,3-dioxolane	bulk	**1**	1.0	−10	24	100			0.19
	1.0	**1**	1.0	−78	24	100			0.14
	bulk	**2**	1.0	−10	24	94			0.16
	1.0	**2**	1.0	−78	24	96			0.10
tetrahydrofuran	bulk	**1**	3.0	28	24	83			0.09
	bulk	**1**	3.0	−10	24	85			0.48
	bulk	**1**	3.0	−78	24	53			0.08
	bulk	**2**	3.0	28	24	–			oligomer
	bulk	**2**	3.0	−10	24	70			0.39

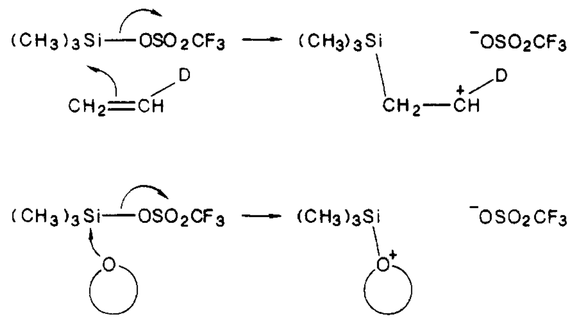
[a] Dichloromethane solvent. [b] Determined as polystyrene equivalents on size exclusion chromatography using chloroform as solvent; three columns (Du Pont Zorbax PSM 300, Du Pont Zorbax PSM 60, and IBM Type A column) and UV (254 nm) or RI detector. [c] Calculated according to ref 13. [d] Performed in $CHCl_3$ at 30 °C at a concentration of 1 g of polymer in 100 mL of solution.

temperatures as low as −78 °C and provide monomodal polymers in high molecular weight.

Polymerizations are run under a nitrogen atmosphere in septum-capped polymerization tubes at the indicated temperature; the yields were determined gravimetrically. For the more reactive monomers such as *N*-vinylcarbazole and *p*-methoxystyrene, the polymerizations were complete in times as short as minutes. The polymerization of the other vinyl monomers and the oxacyclic monomers proceeded more slowly.

Triisopropylsilyl triflate (**2**) is also very reactive with the very electron-rich monomers but gave slower initiation than **1**, in keeping with its greater steric hindrance. This led to somewhat broader molecular weight distribution. This demonstrates control of the reactivity of these initiators with the steric bulk of the silyl fragment. The trialkylsilyl group has already been described as a "bulky proton."[11]

The initiation mechanisms are thought to be



Notice that β-trimethylsilyl groups are well-known to stabilize carbenium ions by hyperconjugative electron release, thus facilitating these initiation reactions.[12] Propagation and termination reactions are presumed conventional.

Advantages of these readily available trialkylsilyl triflates over conventional cationic initiators include ready availability, ease of handling, solubility in organic solvents, high reactivity, lack of aggregation, lack of need for protic cocatalysts, and control of reactivity by varying steric bulk.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society for support of this research.

Registry No. **1**, 27607-77-8; **2**, 80522-42-5; poly(*N*-vinylcarbazole), 25067-59-8; poly(*p*-methoxystyrene), 24936-44-5; poly(isobutyl vinyl ether), 9003-44-5; poly(α-methylstyrene), 25014-31-7; polystyrene, 9003-53-6; trioxane (homopolymer), 9002-81-7; cyclohexene oxide (homopolymer), 25702-20-9; cyclohexene oxide (SRU), 32146-09-1; 1,3-dioxolane (homopolymer), 25067-64-5; tetrahydrofuran (homopolymer), 24979-97-3; tetrahydrofuran (SRU), 25190-06-1.

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Received October 20, 1986