Polymer Bulletin 2, 131–135 (1980)

Polymer Bulletin

Cationic Polymerization of Cyclopentadiene Initiated by Bifunctional Trityl Salts

Evidence for a Direct Addition of the Initiator and Application to Block Copolymerization

M. Villesange, G. Sauvet, J. P. Vairon and P. Sigwalt

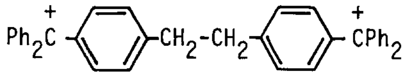
Laboratoire de Chimie Macromoléculaire de l'Université Pierre et Marie Curie,
4, Place Jussieu, 75230 Paris Cédex 05, France

Abstract

A chemical evidence for the fixation of triphenylmethyl cation in the initiation step is given in the case of cyclopentadiene polymerization initiated by stable trityl salts. With $SbCl_6^-$ as counter ion, negligible transfer reaction takes place at 0°C. The situation is more complex with $SbCl_5OH^-$. Mono and bifunctional trityl salts have also been used for the synthesis of AB and ABA block copolymers.

Introduction

Direct addition of a cation to the double bond is the most generally admitted mechanism for initiation of cationic polymerization of vinyl or ethylenic monomers by stable organic salts like trityl or tropylium derivatives (1). Evidences were provided for this mechanism using spectroscopic end groups determinations (2,3,4). Nevertheless, the presence of salt residues in the polymer chain might also result from termination reactions. In order to determine conclusively the mechanism of initiation (direct addition, hydride transfer, or electron transfer from monomer), we initiated the polymerization of cyclopentadiene (CPD) -for which transfer processes are very low or even negligible (5)- in CH_2Cl_2 solution by a bifunctional analogue of triphenylmethyl carbenium ion:



(noted D^{++} in text)

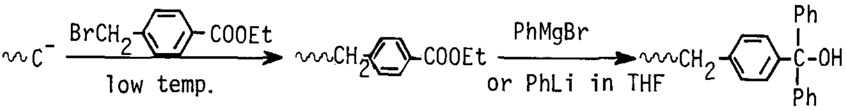
This salt was previously used by KUNTZ (6) in order to show that initiation of THF polymerization proceeded essentially through hydride transfer, whereas FRANTA et al (7), using a similar approach, proved the direct addition of oxocarbenium ions onto THF.

Experimental

* Bifunctional salts D^{++} -4,4'-bis (diphenylmethylcarbenium)bibenzyl bis (antimonyhexachloride) and bis (antimony hydroxypentachloride) - were respectively prepared by addition of a solution of $SbCl_5$ to solutions of the corresponding chloride and carbinol in CH_2Cl_2. These last compounds were synthetised from bibenzyl using a method derived from SLOAN and VAUGHAN (8). The two salts, referred as $D^{++}(SbCl_6^-)_2$ and $D^{++}(SbCl_5OH^-)_2$ were purified by se-

0170-0839/80/0002/0131/$01.00

veral precipitations in hexane.
* Macromolecular mono and bis salts were prepared from mono and bifunctional living anionic poly-α-methylstyrene chains (respectively initiated by cumyl$^-$K$^+$/THF and by Na/THF), through the following sequence of reactions



After precipitation and purification, the macrocarbinol is transformed into the corresponding salt by addition of $SbCl_5$ to a CH_2Cl_2 solution.

Results

Electronic spectra of D^{++} and macromolecular salts differ noticeably from that of Ph_3C^+(Figure 1) and agree with reported λ_{max} for monoparasubstituted triphenyl methyl carbenium ions (9). Apparent molar extinction coefficients of the various salts were determined in CH_2Cl_2 either by simple weighting or by adding to a solution of the corresponding precursor successive increments of a titrated solution of $SbCl_5$, until a plateau is reached. This second method leads simultaneously to ε value (slope) and to the final concentration of functionalized species (plateau). It appears on Figure 1, first that the shape of the absorption peak of the bis salt varies with molecular weight, and second that the oscillator strength f ($f = 4{,}317.10^{-9} \int \varepsilon \, d\nu$) is strongly affected (divided by a factor of ∼ 2) when increasing MW from D^{++} to $\overline{M}_n = 80{,}000$. For each copolymerization experiment we specifically used the ε_{460} of the corresponding macromolecular initiator.

Parallel polymerizations of CPD were performed at 0°C respectively in the presence of monofunctional (Ph_3C^+) and bifunctional (D^{++}) salts, with similar concentrations of monomer and initiating cation (Table 1). Reactions were stopped when at least 90 % of initiator was consumed. When the counter ion is $SbCl_6^-$, comparision of M.W. of the resulting polymers shows that the $\overline{DP}_n$ of the product obtained with D^{++} is about twice the $\overline{DP}_n$ of the product obtained with Ph_3C^+, which proves the direct addition mechanism. A correct and reproducible agreement is observed in this case between the experimental $\overline{DP}_n$ and the theoretical value computed from polymer yield and initial salt concentration.
This is no longer the case for propagation with $SbCl_5OH^-$ counterion. Even if transfer remains low, it may decrease drastically the experimental $\overline{DP}_n$. This is particularly clear for polymerizations initiated by $D^{++}(SbCl_5OH^-)_2$ and it may be seen on Figure 2, that even if the main peak of the G.P. chromatogram corresponds to the expected theoretical molecular weight, the distribution is broadened by a low MW tail. Deviation between experimental and theoretical $\overline{DP}_n$ is less sensitive when using $Ph_3C^+SbCl_5OH^-$ as initiator (Table I). In this case, transfer leads to a larger proportion of low MW chains than in the case of D^{++} $(SbCl_5OH^-)_2$, so that oligomers lost during polymer recovery represent a greater part

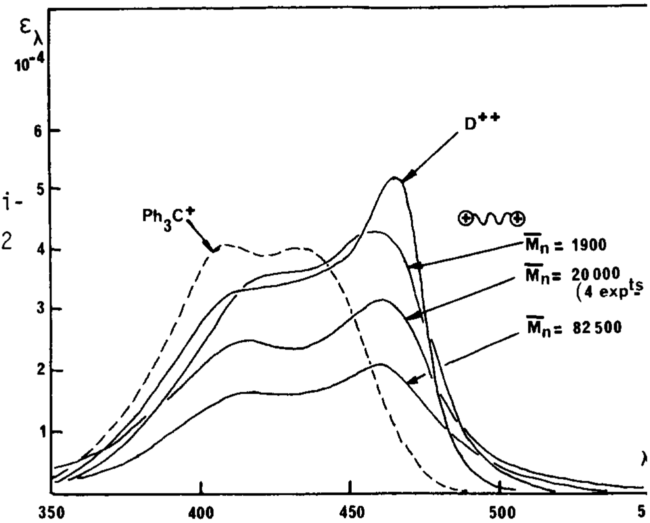


Figure 1:

Electronic spectra of bifunctional trityl salts in CH_2Cl_2 (room temp.)

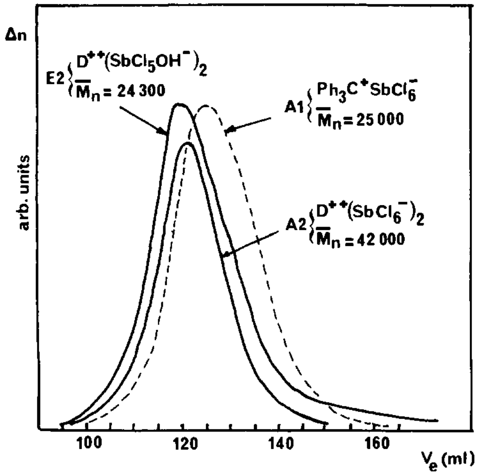


Figure 2:

GP chromatograms of PCPD obtained with $D^{++}(SbCl_6^-)_2$ and $D^{++}(SbCl_5OH^-)_2$

(see text and Table I)
-solvt: THF

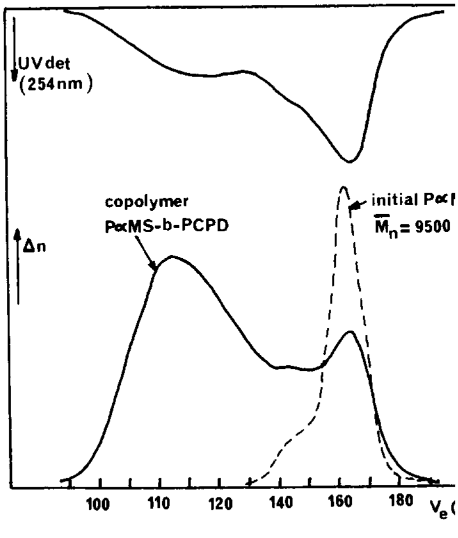


Figure 3:

Example of block copolymerization. GP chromatogram of resulting mixture, expt. M_2
(see Table II)
UV absorption of PCPD at 254nm may be neglected.

of the whole polymer, and thus values of k_p/k_{trm} -computed from theoretical and experimental $\overline{DP}_n$(4) - are probably overestimated. Nevertheless, it appears that these ratios, which are very high or even meaningless with the counter ion ($SbCl_6^-$), are significantly lower with ($SbCl_5OH^-$). This indicates the transfer processes to be more favoured when the growing carbenium ion is associed with $SbCl_5OH^-$ rather than with $SbCl_6^-$, and to occur mainly on ion pairs.

TABLE I

Polymerizations of cyclopentadiene initiated by Ph_3C^+ and D^{++} at 0°C in CH_2Cl_2

Exp.	Initiator	$\|I^+\|_o.10^4$ eq. l^{-1}	$\|M\|_o$ mol.l^{-1}	Y_{pol} %	$\overline{DP}_n$ osm.	$\overline{DP}_n$ theor. *	$\frac{k_p}{k_{trm}}$ **
	$SbCl_6^-$						
A_1	Ph_3C^+	7.5	1.35	20	380	386	very high
A_2	D^{++}	7.6	1.35	20	610	700	4,700
B_1	Ph_3C^+	7.4	1.39	21	430	439	very high
B_2	D^{++}	7.3	1.39	20	670	782	4,900
C	D^{++}	0.93	1.12	4	820	973	5,200
	$SbCl_5OH^-$						
D_1	Ph_3C^+	9.7	0.87	34	290	338	2,000
D_2	D^{++}	9.7	0.87	27	320	490	900
E_1	Ph_3C^+	6.5	1.35	18	350	402	2,700
E_2	D^{++}	7.6	1.35	19	360	668	800

* calculated from yield and consumed initiator (> 90 % $|I^+|_o$), assuming no transfer

** estimated error : ± 10 %.

Block copolymers may be prepared using mono or bifunctional macromolecular initiators of the above type. We synthesized trityl ends from living anionic poly α methylstyrene chains (see Experimental) and the resulting salts were used in A-B and A-B-A copolymerizations with cyclopentadiene. Unfortunately isolation of pure macromolecular triarylchloride (leading to $SbCl_6^-$) appeared technically difficult. Copolymerizations were performed with $SbCl_5OH^-$ counter ion and even if transfer led to some homopolymer, the sequencing efficiency (S.E. = $\frac{\text{PCPD in blocks}}{\text{overall PCPD}}$ %) remained rather high. The k_p/k_{trm} ratios for CPD block copolymerization were computed from the theoretical $\overline{DP}_n$, assuming no transfer, and the experimental one taking into account blocks and homo PCPD chains. Values are somewhat scattered but the order of magnitude is comparable to that observed for polymerization initiated by Ph_3C^+ with $SbCl_5OH^-$ as counterion. Functionalization of anionic polyαmethylstyrene was generally incomplete and copolymers were separated from unreacted initial polymer by recycled preparative GPC (Figure 3). Typical examples are summarized in Table II. We are presently studying these copolymerizations and details will be published elsewhere.

TABLE II

Examples of A-B and A-B-A block copolymerization of cyclopentadiene and poly α-methylstyrene.

T = 0°C $|CPD|_o \sim 2$ mol.l^{-1} solvent = CH_2Cl_2

$Exp^{\underline{t}}$	$Funct^{\underline{y}}$	$\overline{M_n}$ p MS	yield of $funct^{\underline{n}}$	$\lvert I^+\rvert_o.10^4$ mol.l^{-1}	Copolym. weight %	S.E.* %	M_n of PCPD sequences** a	b	k_p/k_t
M_1	∿∿∿⊕	9 500	28	1.9	41	86	9 900	8500	3 00
M_2	∿∿∿⊕	9 500	71	3.3	51	61	32 000	25100	80
M_3	⊕∿∿∿⊕	82 500	100	3.7	96	85	15 800	13400	1 30

* Sequencing efficiency - See text.
** a : theoretical, assuming no transfer
b : experimental (blocks + transfered chains).

References

(1) LEDWITH A., SHERRINGTON D.C., Adv. Polymer Sci. 19, 1, (1975
(2) SAUVET G., VAIRON J.P., SIGWALT P., J. Polymer Sci. A-1, 7, 983 (1968)
(3) BAWN C.E.H., FITZSIMMONS C., LEDWITH A., PENFOLD J., SHERRINGTON D.C., WEIGHTMAN J.A., Polymer, 12 (2), 119 (1971
(4) COTREL R., SAUVET G., VAIRON J.P., SIGWALT P., Macromolecules 9, 931 (1976)
(5) SAUVET G., VAIRON J.P., SIGWALT P., Europ. Polymer J. 10, 501, (1974)
(6) KUNTZ I., J. Polymer. Sci. A-1, 5, 193 (1967)
(7) FRANTA E., REIBEL L., LEHMAN J., PENCZEK S., J. Polymer Sci. Symposium 56, 139 (1976)
(8) SLOAN G.J., VAUGHAN W.R., J. Org. Chem. 22, 750 (1957)
(9) OLAH G.A., PITTMAN C.U. Jr., SYMONS M.C.R., Chapt. 5 in "Carbonium Ions" Vol. I, OLAH G.A. and Von R. SCHLEYER P. Edrs. Wiley Interscience 1968

Received December 6, 1979