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CATIONIC INITIATION BY THIONYL CHLORIDE/TITANIUM TETRACHLORIDE. II. STYRENE POLYMERIZATION

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ABSTRACT

The thionyl chloride/titanium tetrachloride combination in methylene chloride solution is found to be a good cationic initiating system for styrene polymerization. The efficiency of the initiation is governed by the amount of titanium chloride used. It was found by the IMA and AMI techniques that the system possesses a partially living character, and the polystyrenes obtained exhibit some stereoregular structure.

INTRODUCTION

In searching for new initiating systems, we found that the combination of thionyl chloride (SOCl_2) with titanium tetrachloride (TiCl_4) is an efficient initiator of cationic olefin polymerizations.

Thus, model reaction studies [1] with tetraphenylethylene (TPE) and 1,1-diphenylethylene (DPE) showed that the final products were symmetric sulfoxide derivatives of the R-S-R type. The ionic character of the initiation step has been



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demonstrated by the sudden increase of the conductivity when initiator and monomer solutions are brought together.

In this paper we report the study of styrene polymerization initiated by the $\text{SOCl}_2/\text{TiCl}_4$ combination in CH_2Cl_2 solution in the temperature range from -70 to 25°C .

EXPERIMENTAL

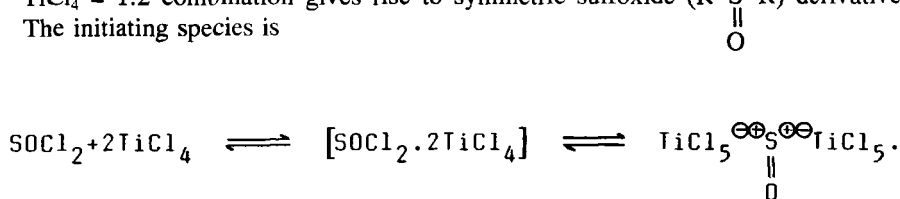
Vacuum-line techniques were used for the purification of the reactants and to carry out the polymerizations. CH_2Cl_2 was distilled twice under vacuum from P_2O_5 . Styrene (St) was first distilled under reduced pressure, stored over Molecular Sieves and distilled under vacuum before use. SOCl_2 and TiCl_4 were vacuum distilled before use.

Polymerizations were carried out as follows: A solution of styrene was introduced into an all-glass reactor equipped with a magnetic stirrer, and the system was cooled to the desired temperature. A solution of initiator was added and, after 30 min, the reaction was stopped by introducing an ammoniacal methanol solution. The resulting polystyrenes (PS) were purified by repeated precipitation with methanol.

A Bruker 200 SY NMR spectrometer was used for polymer analysis. Molecular weights of the PS samples were determined by viscometry in toluene at 25°C . To the evaluation, the relations reported for benzene at 25°C : $[\eta] = 10^{-3} \bar{M}_v^{0.50}$ for $\bar{M}_v < 10^4$ and $[\eta] = 4.2 \times 10^{-4} \bar{M}_v^{0.60}$ for $\bar{M}_v > 10^4$ [2] were used as approximations. In some cases the molecular weights were also determined by GPC (Waters) in THF.

RESULTS AND DISCUSSIONS

It is known that SOCl_2 alone cannot initiate the polymerization of styrene [3, 4]. However, in our paper dealing with model reactions [1], we showed that a $\text{SOCl}_2/\text{TiCl}_4 = 1:2$ combination gives rise to symmetric sulfoxide ($\text{R}-\text{S}-\text{R}$) derivatives. The initiating species is



Therefore, in our experiments with styrene, we used this ratio. We found that the polymerization of styrene is fast (76% conversion in the first minute) even at 25°C . Table 1 shows the temperature dependence of the conversion.

TABLE 1. Temperature Dependence of Styrene Polymerization in CH_2Cl_2

Run	[St], mol/L	[I], mmol/L	T, °C	Conversion, % (1 min)	\bar{M}_v
1	1	13	25	76	5 600
2	1	11	0	80	10 900
3	1	13	-30	83	11 900
4	1	12	-50	82	18 800
5	1	11	-70	85	22 100

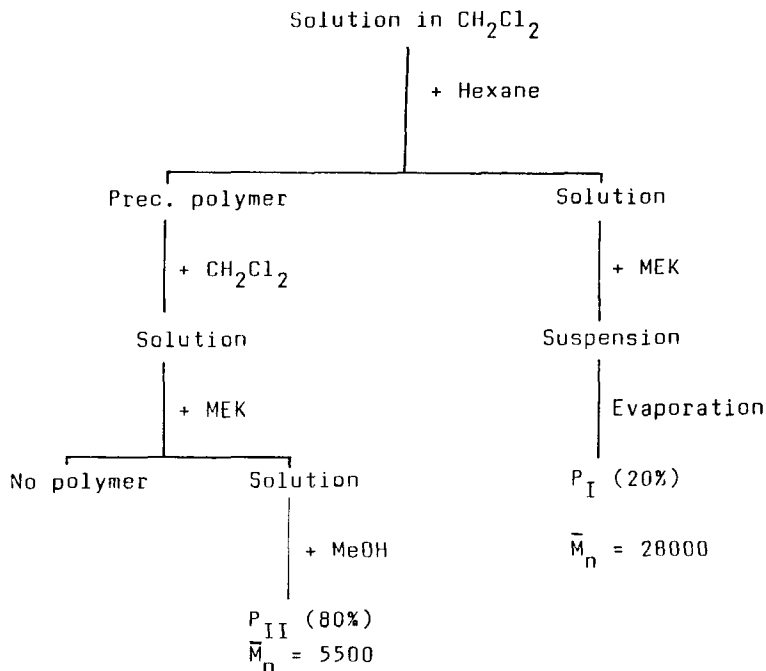
The molecular weight increases with decreasing temperature. Figure 1 shows that this dependence is practically linear. Using AMI (All Monomer In) and IMA (Incremental Monomer Addition) techniques (see, e.g., Ref. 5), we investigated whether the system is living or not. The results are summarized in Table 2. The plot (Fig. 2) of molecular weight vs amount of polymer formed (W_p) shows an increase of \bar{M}_v with W_p .

In view of the question of the living character of the system, some GPC determinations of the PS samples were carried out. The GPC traces were bimodal. This fact and the deviation from the linearity in Fig. 2 indicate that side reactions occurred and that the system is only partly living.

Another proof of the living character comes from one-pot copolymerization experiments. A solution of styrene (0.33 mol/L) was allowed to polymerize for 10 min at -70°C , and then a solution of isobutylene (0.43 mol/L) was added. After 20 min the reaction was stopped by introducing MeOH. The polymer was purified by repeated precipitation with MeOH. GPC analysis indicated two distinct peaks, corresponding to \bar{M}_n 5500 and 28 000. This polymer was submitted to a fractionation, as shown in Scheme 1.

Since PS is soluble in methyl ethyl ketone (MEK) and insoluble in hexane, and PIB is soluble in hexane and insoluble in MEK, the solution obtained after hexane addition should contain homo-PIB which should be precipitated by MEK addition. In fact, we obtained only a suspension which, after evaporation, gave P_I . The polymer precipitated by hexane addition was also soluble in MEK, indicating that no homo-PIB was present. This result confirms our earlier finding that $\text{SOCl}_2/\text{TiCl}_4$ does not initiate IB polymerization [1]. P_{II} is obtained only by precipitation in MeOH. ^{13}C -NMR analysis showed that P_I is a block copolymer of styrene and isobutylene (Fig. 3) and that P_{II} is a homopolystyrene.

The fact that only 20% of the product is copolymer indicates the occurrence of transfer reactions. Thus, we can conclude that the system is only partially living.



SCHEME 1. Fractionation scheme.

According to ^{13}C -NMR spectra, PS samples obtained in this system exhibit some microtacticity. As shown in Fig. 4, three triads in the methine resonance range of 40–50 ppm can be distinguished, corresponding to *rr*, *mr*, and *mm* structures. This stereoregularity can be seen also in the phenyl-C region (*rr* = 146.1, *mr* = 145.7, and *mm* = 146.1 ppm). We estimate, for example, that about 20% *mm*, 40% *mr*, and 40% *rr* are present in a PS obtained at -30°C .

Generally, polystyrenes and derivatives are mainly syndiotactic [5, 6] when polymerized with Friedel-Crafts initiators (BF_3 , $\text{BF}_3 \cdot \text{OEt}_2$, TiCl_4 , SnCl_4), particularly in polar solvents. However, the low value obtained in our case fits well with that obtained by Matsuzaki et al. [7], who used PF_5 as initiator. This may be explained by the difference of the growing ion-pair in the propagation step. As suggested by Lenz et al. [5], an S_N1 -like propagation reaction (one growing species) leads to syndiotactic polymer. In case of an S_N2 -like reaction, the existence of two stereo-isomeric growing

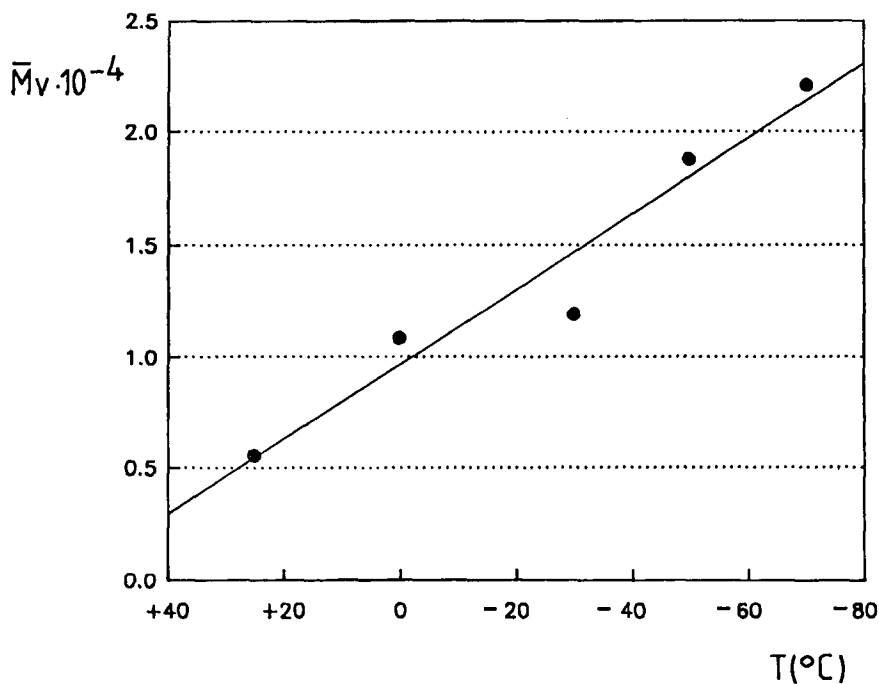


FIG. 1. Influence of temperature on the polymerization of styrene ($[M] = 1 \text{ mol/L}$, $[I] = 11\text{--}13 \text{ mmol/L}$).

TABLE 2. Styrene Polymerizations in CH_2Cl_2 by the AMI and IMA Techniques^a

Technique	Run	$[\text{St}]$, mol/L	\bar{M}_v	Conversion, %	W_p ^b g
AMI	6	0.5	12 200	77	0.40
	7	1.0	22 100	91	0.95
	8	1.5	29 000	90	1.40
	9	2.0	30 200	91	1.90
IMA	10	1.0	24 800	96	1.00
	11	1.5	32 000	96	1.50

^aTemperature -70°C ; $[I] = 11.3 \text{ mmol/L}$; total volume 10 mL.

^b W_p = weight of PS in 10 mL solution.

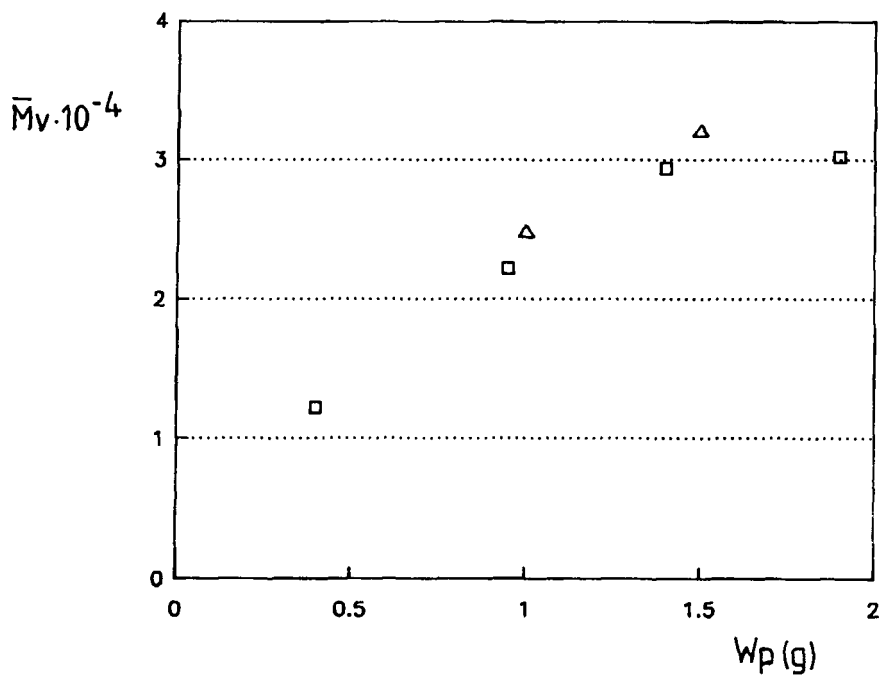


FIG. 2. Molecular weight as a function of polymer yield for styrene polymerization: (Δ) AMI, (\square) IMA, temperature -70°C , $[\text{I}] = 11.3 \text{ mmol/L}$.

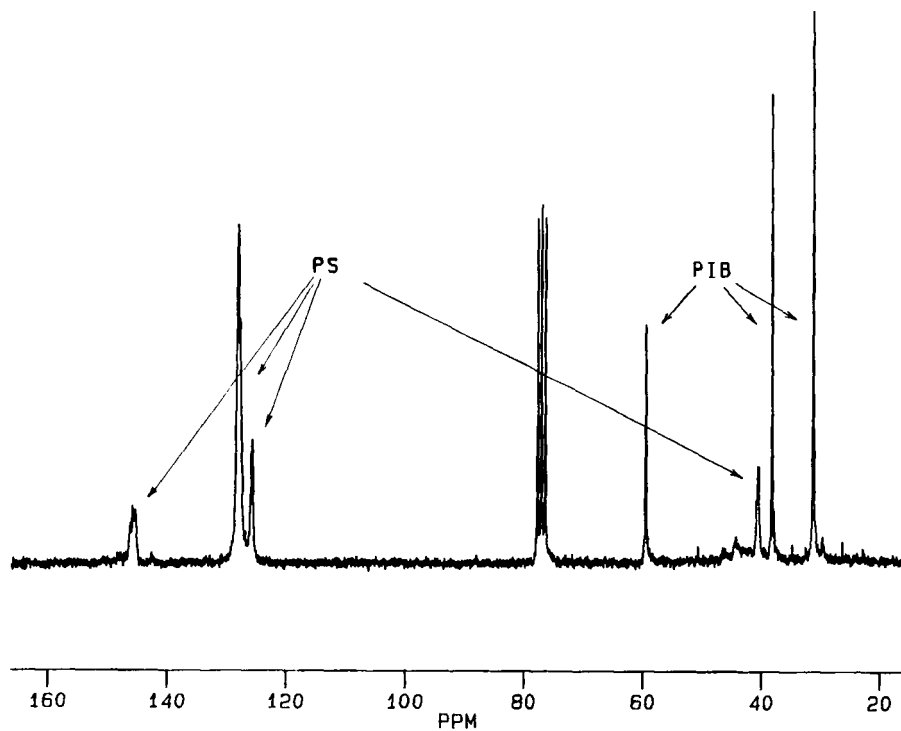


FIG. 3. ^{13}C -NMR spectrum of P_1 (styrene-isobutylene block copolymer) in CDCl_3 .

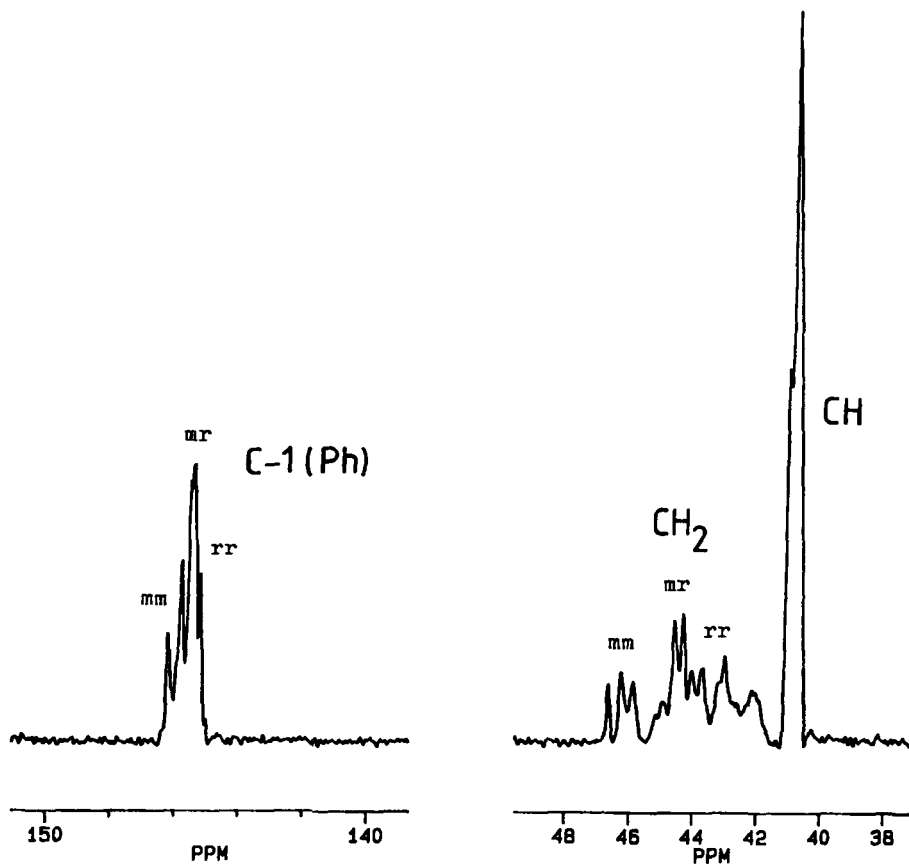


FIG. 4. ^{13}C -NMR spectrum of a polystyrene (exhibiting some microtacticity) in CDCl_3 .

chain species has to be considered, and the probability of the formation of a less syndiotactic polymer is higher.

CONCLUSIONS

In conclusion, we have shown that the $\text{SOCl}_2/\text{TiCl}_4$ combination is an efficient initiator for styrene polymerizations. In spite of side reactions, the system partially possesses a living character. Based on our results obtained with model reactions, we can assume that the polymer molecules have a sulfoxide group in the middle of the chain (PS-S-PS). However, elementary analysis did not give reproducible results,



especially in respect to the sulfur content.

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