Eur. Polym. J. Vol. 20, No. 6, pp. 619–623, 1984
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0014-3057/84 $3.00 + 0.00

POLYMERIZATION OF SUBSTITUTED OLEFINS INITIATED BY ORGANOMETALLIC COMPOUNDS OF TITANIUM (IV)—II

EVIDENCE FOR A PREDOMINANT RADICAL PROCESS WITH METHYLTITANIUM DERIVATIVES

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(*Received* 15 *July* 1983)

Abstract—Polymerizations of methyl methacrylate (MMA), vinyl acetate, acrylonitrile or styrene (St) initiated by methyl derivatives of Ti(IV) are consistent with a radical process. This conclusion is supported by tacticities of the resulting polymers which are close to those for conventional radical samples and show that propagation obeys a Bernoullian statistics. The major evidence is provided by statistical MMA–St copolymerization which clearly exhibits radical reactivity ratios.

INTRODUCTION

Titanium derivatives, most generally associated with alkylaluminium compounds, are extensively used as Ziegler–Natta catalysts to initiate the polymerizations of ethylene and vinyl monomers. Although the presence of a titanium–alkyl bond formed *in situ* (with or without reduction of titanium IV to titanium III) is thought to play a predominant role in the catalytic process, very little is known about the polymerization of ethylenic monomers initiated by well defined σ-bonded organometallic titanium IV derivatives.

Since the pioneering and extensive studies of Giannini [1, 2] and Ballard [3–5] with benzyl derivatives of Zr and Ti, it has been shown that alkylorganotitanics prevented from β-elimination (methyl or β-substituted) may act as polymerization initiators for various ethylenic monomers. Ballard proposed a radical mechanism for styrene and methyl methacrylate polymerization when benzyl Ti or Zr are irradiated at their absorption wavelength and a Ziegler–Natta type mechanism (insertion into the C-Mt bond) when irradiated at higher wavelength or in the dark. Characterized methyl and neopentyl derivatives of transition metals and particularly Ti(IV) were reported to be active either under photolysis conditions [6–8] or without any irradiation [8, 9]. For photochemical initiation, most results and conclusions (based on kinetics, EPR, stereostructure of polymers) support a radical process even if the simple homolytic scission of the σ-Ti-C bond might eventually be questioned [6]. The situation is more obscure when the polymerizations are performed in the dark or in daylight. Koide [9] and then Chien [8] observed that DPPH was ineffective or increased the rate leading these authors to discard a radical process or to propose a caged radical propagation.

We previously reported [10] the ability of various alkoxy derivatives of titanium IV to initiate the polymerizations of ethylenic monomers such as methyl methacrylate (MMA), vinyl acetate (VAc), acrylonitrile (AN), styrene (St). The polymerizations were mainly performed in bulk and the results (Ref. 10, Table 2) clearly showed that, in the case of MMA, the initiating efficiency is related to the presence of a methyl group bonded to the titanium whereas, in the case of styrene, the activity of these methyl derivatives remains low and comparable to those of diethyl amido or benzyl derivatives. Even if the reactions were not followed kinetically, the polymerization systems with CH_3-Ti(IV) compounds as initiators behave similarly in daylight or in darkness. Nevertheless most of the qualitative features of these systems seemed to support a radical mechanism and led us to re-examine and complete our results in the light of polymer structure and copolymerization reactivities. We now report our conclusions.

EXPERIMENTAL

Reagents

Monomethylalkoxy derivatives of Ti(IV), i.e. $CH_3Ti(OR)_3$ and $CH_3Ti(C_5H_5)(OR)_2$, were synthesized at about $-20°$ in diethyl ether solution under inert atmosphere by reacting either CH_3Li with the corresponding Cl-Ti(IV) precursor, or CH_3MgI with $Ti(OR)_4$ or with $(C_5H_5)Ti(OR)_3$. They were purified by distillation under high vacuum (0.02–0.1 torr) and characterized by ^1H-NMR and mass spectrometry. The dimethyl $(CH_3)_2Ti(IV)$ compound obtained by stoichiometric reaction of $CH_3Ti(OR)_3$ with

$Al(CH_3)_3$ was shown to be the μ-alkoxo-bridged binuclear complex in equilibrium with dissociated species:

$$[(CH_3)_2(RO)Ti(\mu\text{-}OR)_2Al(CH_3)_2] \rightleftarrows (CH_3)_2Ti(OR)_2 + 1/2[(RO)Al(CH_3)_2]_2$$

Details concerning these syntheses are reported elsewhere [11]. Monomers and solvents were distilled and stored over molecular sieves. All reagents were outgassed before use by freezing–melting cycles under vacuum.

Polymerization procedures

Polymerizations and copolymerizations were generally carried out in bulk at 25° under argon or nitrogen with a monomer-to-catalyst molar ratio of 40:1, by adding the monomer to the freshly prepared initiator. The medium was stirred until it became too viscous and, after ~2 days of reaction, the solid polymer was dissolved and precipitated in a suitable precipitant. This operation was repeated several times in order to remove the catalyst residues. The course of the polymerization was in some cases followed by ^{1}H-NMR.

Polymer characterization

The composition of poly(St-co-MMA) was determined from the aromatic-to-aliphatic protons ratio of the ^{1}H-NMR spectra. Tacticities of homopolymers were mainly evaluated from ^{13}C-NMR spectra recorded with conventional or high field instruments (25 and 63 MHz, Jeol PFT and Bruker WM 250). PMMA, PSt and PVAc samples were examined as 15% w/v solutions in $CDCl_3$ at 40°. PAN samples were examined in DMSO d_6. TMS was the external standard.

RESULTS

Poly(methyl methacrylate)

Whatever the methyl titanium derivative used, the bulk polymerizations are complete within 48–55 hr and exhibit marked autoacceleration in the second half of the reaction (Fig. 1). If the polymerization is carried out in $CHCl_3$ solution, this effect disappears and after 48 hr the conversion is about 50%. The use of a solvent which has not been previously outgassed and thus deoxygenated led to a drastic reduction of the reaction. Complete conversions of MMA were also observed when operating in bulk with ~200:1 monomer-to-catalyst ratio.

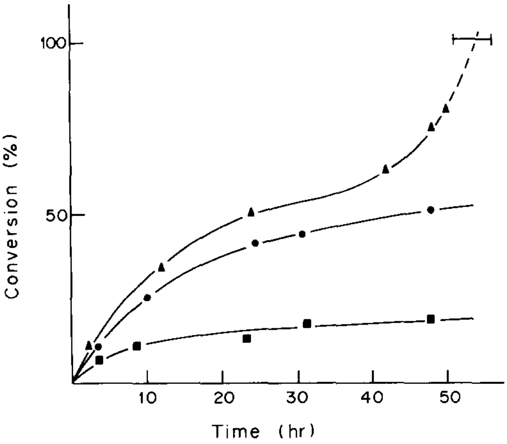

Fig. 1. Conversion curves for MMA polymerization at 25°. (▲) Bulk, CH_3Ti $(O\text{-}iPr)_3$ + MMA (40:1 molar respect to titanium derivative). (●) Solution, $CH_3Ti(O\text{-}iPr)_3$ + MMA (40:1) + $CHCl_3$ (40:1). (■) Solution, not degassed—same concentrations as above.

Molecular weights and yields obtained at various polymerization temperatures are reported in Table 1. An increase of the yield and a decrease of $\bar{M}_w$ with elevation of T are observed when the binuclear complex is used. A reverse variation of $\bar{M}_w$ is obtained with the monometallic system, whereas conversion is incomplete at 55°.

Tacticities of PMMA expressed in rr, mr, mm triads distributions were obtained either from the carbonyl or from the α-CH_3 carbon resonances

Table 1. Influence of polymerization temperature on molecular weights and yields of PMMA obtained in bulk

Initiator	T (°C)	$\bar{M}_w$*	Yield (%) after 2 days
$CH_3Ti(O\text{-}iPr)_3$, $Al(CH_3)_3$	−18	1.0×10^5	40
$CH_3Ti(O\text{-}iPr)_3$, $Al(CH_3)_3$	25	3.2×10^4	100
$CH_3Ti(O\text{-}iPr)_3$, $Al(CH_3)_3$	55	2.8×10^4	100
$CH_3Ti(O\text{-}iPr)_3$	−18	7.0×10^4	30
$CH_3Ti(O\text{-}iPr)_3$	25	2.1×10^5	100
$CH_3Ti(O\text{-}iPr)_3$	55	8.5×10^5	75

*As determined by viscometry in benzene at 30° using the $|\eta|_{dl\,g^{-1}} = 5.2 \times 10^{-5}\,\bar{M}_w^{0.76}$ relationship [12].

Table 2. Microstructure of PMMA obtained in bulk with methyl and diethyl-amido organotitanium derivatives ($m/c = 40$, $T_{pol.} = 25°$)

Initiator	Conversion after 2 days (%)	Microstructure (%)			$4is/h^2$	σ
		mm	mr	rr		
$CH_3Ti\ (OiPr)_3$	100	5	34	61	1.05	0.22
$CH_3Ti\ (OtBu)_3$	100	2	32	66	0.51	0.19
$(C_5H_5)Ti(OCH_2CF_3)_2/CH_3)$	100	1	30	69	0.31	0.17
$CH_3Ti(OiPr)_3$, $Al(CH_3)_3$	100	4	31	65	1.08	0.19
$(Et_2N)Ti(OiPr)_3$*	16	3	31	66	0.82	0.19

*Prepared as described in the literature [16].

Table 3. Microstructures of PAN and PVAc (polymerization conditions as in Table 2)

Polymer	Initiator	Conversion after 2 days (%)	Microstructure (%) mm	mr	rr	$4is/h^2$	σ
PAN	$CH_3Ti(OiPr)_3,Al(CH_3)_3$	100	29	50	21	0.97	0.54
	$CH_3Ti(OiPr)_3$	10	26	50	24	0.99	0.51
	$(Et_2N)Ti(OiPr)_3$	100	29	42	29	1.91	—
	litt. (redox)*	—	31	48	21	1.13	0.54
PVAc	$CH_3Ti(OiPr)_3$	100	27	(48 + 25)***		(1.17)	(0.52)
	litt.**	—	20.7	49.7	29.6	0.99	0.46

*Ref. 17. **Ref 18. ***Overlapping of pentads makes questionable the resolution of the upfield peaks of the α-CH resonance pattern.

(Table 2). They appear similar for all samples whatever the initiator even for the diethyl-amido compound, and they agree with Bernoulli trial distribution, the deviations below unity of the (4 is/h^2) ratio resulting obviously from the lack of accuracy for the low (mm) values. Such microstructures (and σ values) are consistent with those observed for free radical and free anion propagation [13–15] or those obtained in bulk polymerization of MMA initiated by $(Neopentyl)_4$ Ti with or without irradiation [8].

Poly(acrylonitrile) and poly(vinyl acetate)

VAc, which is known to polymerize by a radical process, is readily converted by the CH_3-Ti(IV) initiator. In the case of AN, complete conversions after 48 hr are also obtained with the diethyl-amido and the binuclear methyl derivatives whereas the yield remains low with the monomethyl compound. Tacticities of PAN and PVAc were evaluated from the α-methine carbon resonances centred respectively at 27.6 and 66.7 ppm. Samples polymerized with the CH_3-Ti(IV) initiators appear very similar to the free radical polymers but the PAN initiated by the amido compounds exhibits a deviation which might be significant (Table 3).

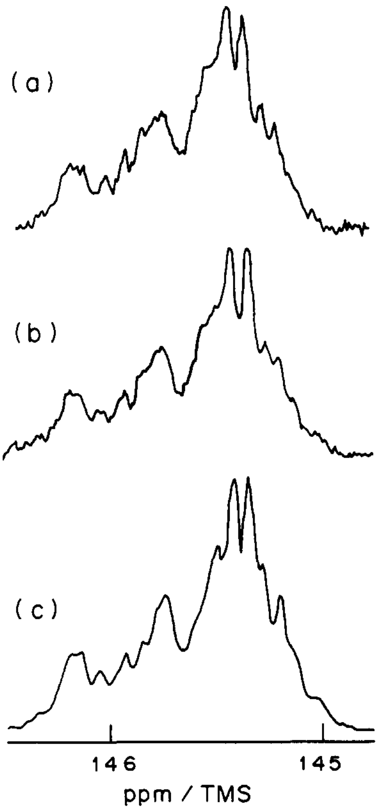

Fig. 2. 63 MHz ^{13}C-NMR resonance patterns of C_1 aromatic carbons for different polystyrenes ($CDCl_3$, 40°). (a) Initiation by $CH_3Ti(O\text{-}iPr)_3$. (b) Initiation by $C_6H_5CH_2Ti(O\text{-}iPr)_3$. (c) Emulsion ($S_2O_8K_2$, 70°).

Polystyrene

We previously reported [10] that, using the same experimental conditions, the above initiators and the monobenzyl derivative lead to low conversions of styrene (11–20%). Microstructures of the polymers, examined through the resonance pattern of the aromatic quaternary carbon C_1, appear very similar for samples initiated by mono or binuclear CH_3-Ti(IV) derivatives as well as for samples initiated by diethylamido or benzyl compounds. The triads distribution was estimated by using the last assignment of Matsuzaki [19] and dividing the C_1 patterns in four blocks respectively attributed to (mmmm + mmmr), (mrmm + mmrr), (rrmr + mrmr + rmmr) and (rr) stereosequences. The lack of resolution due to the complex overlapping, in addition to an always questionable assignment, allows only a rough approxi-

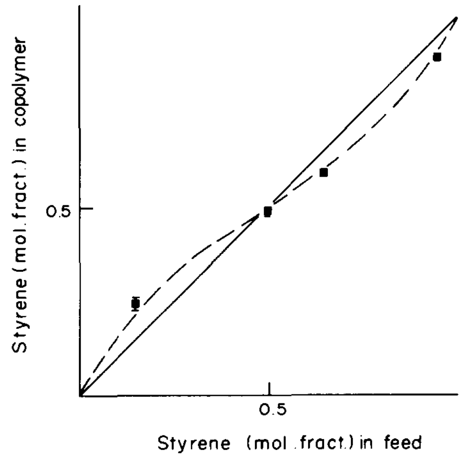

Fig. 3. Composition of [St-*co*-MMA] copolymers. Copolymerization initiated by $CH_3Ti(O\text{-}Pr)_3$ at room temperature in bulk. (■) Statistical copolymer. (--) Theoretical curve corresponding to a free radical copolymerization. $r_{St} = 0.511$, $r_{MMA} = 0.488$. Kelen–Tüdős [20], from Mayo–Lewis results [21].

mation of the (rr) triad which, assuming Bernoullian statistics, leads to a (rr) = 0.28, (mr) = 0.50, (mm) = 0.22 distribution with a P_r (= 1-σ) of 0.53. This is very close to the microstructure of free radical polystyrene as shown in Fig. 2 which compares our polymers with an emulsion polystyrene (|rr| = 0.32, |mr| = 0.49, |mm| = 0.19, P_r = 0.57, by the same method).

Copolymerization of methyl methacrylate and styrene

Copolymerizations were carried out at room temperature using the same conditions as for homopolymerizations and the catalyst was $CH_3Ti(OiPr)_3$. The reactions were stopped after 5 hr and conversions were all in the 3–5% range. Instantaneous copolymer compositions vs comonomer feed compositions, expressed in molar fraction, are given on Fig. 3. They fit well with the theoretical composition curve for a free radical process.

DISCUSSION

This paper is mainly concerned with mono or dimethyl derivatives of Ti(IV). The general behaviour of the polymerization systems when using these initiators is consistent with a radical process. This is, at first, strongly supported by the complete bulk polymerization of MMA, with marked autoacceleration which can be suppressed by adding an equimolar amount of solvent, and by the ability to polymerize VAc. Tacticities of PMMA, PVAc and PAN obtained with the methyl derivatives are very close to those observed with a conventional radical initiator and show that, in all cases, the propagation obeys Bernoullian statistics. But the major evidence is provided by the statistical MMA–St copolymerization which clearly exhibits radical reactivity ratios. As we did not test the effect of DPPH on the polymerization, we are unable to decide if the mechanism is a simple radical process or a "coordinated radical" one as proposed by Chien [8] in the case of $(Neo)_4Ti$. It is interesting to note that the St–MMA copolymerization system behaves quite differently with CH_3-Ti(IV) derivatives and with $(Bz)_4Zr$ in the dark for which Ballard first [4, 5] and very recently Martineau [22] obtained a strong enrichment in MMA units. This latter author, who also observed by GPC a small amount of a radical type copolymer, proposed for $(Bz)_4Zr$ an anionic mechanism superimposed on a minor radical process.

Nevertheless, and even if a radical process is obviously dominant, the exclusiveness of this mechanism might be questionable. All our observations are not strictly coherent as for example the difference in behaviour with respect of temperature for polymerizations initiated by dimethyl and monomethyl Ti(IV) compounds (Table 1). The binuclear initiator leads to $\overline{M}_w$ and yield variations in agreement with a radical propagation which is not the case for the mononuclear initiator. Even if $\overline{M}_w$ measurements on high conversion polymers prepared in bulk are not very valuable, an explanation which involves a radical process in both cases might be the significant difference in thermal stability between the two compounds [23] as uncontrolled decomposition of the less stable mononuclear $CH_3Ti(OR)_3$ derivative could occur upon preparation and handling leading thus to the highest $\overline{M}_w$ and incomplete conversion observed for polymerization of MMA at 55°. This might also explain the low AN conversion observed with this catalyst (Table 3).

To sum up the results for the well defined mono or dimethyl Ti(IV) initiators, it seems clear that, in daylight or in the dark, a radical process is predominant for MMA, VAc and AN. The low conversions observed with styrene agree also with the large difference in reactivity, compared to MMA, which is observed in radical polymerization for these two monomers ($k_{pMMA}/k_{pSt} \sim 6$, extrapolation at 25° from Arrhenius plots [24]).

For polymerizations initiated by the dialkylamidotitanium derivative, our results support the previous reports for the same type of catalyst. For MMA (or St) polymerization at 25°, radical mechanism was proposed [25] which might agree with the Bernoullian stereosequences distribution of our PMMA sample (Table 2). An anionic [25] and a coordinate insertion mechanisms [26, 27] were proposed for AN polymerization and, if the tacticity of our corresponding PAN sample allows a radical process to be discarded, we are unable to decide between a pure anionic and a coordinated propagation.

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Résumé—La polymérisation du méthacrylate de méthyle (MMA), de l'acétate de vinyle, de l'acrylonitrile ou du styrène (St), amorcée par des dérivés méthylés du Ti(IV), résulte d'un processus radicalaire. La tacticité observée sur les polymères correspondants est voisine de celle d'échantillons radicalaires conventionnels et montre que la propagation obéit à une statistique Bernoullienne. Mais l'évidence la plus nette est apportée par la copolymérisation statistique MMA–St qui conduit à des réactivités analogues à celles observées en copolymérisation radicalaire de ces deux monomères.