required by the stoichiometry of eq 3, the yield of inorganic phosphate equals that of Schiff base. When *o*-trifluoromethylaniline was substituted for aniline, similar reactions were observed. Furthermore, control experiments show that the process does not occur by phosphorylation of carbinolamine or by way of enol phosphate. *sec*-Phenethyl alcohol is a reasonable model for the carbinolamine and should, if anything, be more mucleophilic than the latter. Furthermore, the carbinolamine must be present in solution in only low concentration.[1] Yet, 5 mol % (relative to acetophenone) of *sec*-phenethyl alcohol had no detectable effect on the yield of Schiff base or inorganic phosphate.

Finally, monomeric metaphosphate anion promotes the amidation of ethyl acetate in the presence of aniline to yield ethyl *N*-phenylacetimidate. The reaction presumably occurs as shown in eq 4; the direct reaction between aniline and the ester yields acetanilide. Monomeric metaphosphate anion activates the ester for attack by amine;[12] the tetrahedral intermediate then undergoes elimination. As required by the common intermediate, the yields of inorganic phosphate and imidate are within experimental error. The reaction to produce imidate is unlikely to require phosphorylation of the tetrahedral intermediate that must lie on the pathway to acetanilide. That intermediate is presumably present in solution, but its concentration must be minute[13] relative to that of the isopropyl alcohol added in a control experiment; the alcohol did not appreciably diminish the yield of imidate.

Interestingly, the amidation of ethyl benzoate (which was successeful with monomeric methyl metaphosphate) fails with PO_3^-. Presumably, the ester-PO_3^- adduct formed with ethyl acetate is more efficiently trapped by aniline than is the adduct formed with ethyl benzoate; on both electronic and steric grounds the former adduct is expected to be more highly activated at carbon for reactions with nucleophiles. If the intermediate is not promptly trapped, it probably reacts with aniline to yield the phosphoramidate.

Enzymology. Both formation of enol phosphate and the amidation described above find parallels in enzyme-catalyzed reactions which require adenosine triphosphate (ATP).[3] "High-energy" phosphates including ATP could serve as sources[14] for monomeric metaphosphate anion. Pyruvate kinase catalyzes the reversible formation of phosphoenol pyruvate from pyruvate and ATP, while CTP synthetase promotes ATP-dependent amidation (O^{18} studies[15] demonstrate overall phosphorylation at the oxygen atom of the carbonyl group in the course of this latter reaction). Both of these examples, as well as others, have been discussed previously.[1] Although the chemical reactions reported above provide evidence for a direct reaction of monomeric metaphosphate anion with the carbonyl oxygen group, the enzyme-catalyzed reactions may, but need not necessarily,[16] proceed by attack of ATP on the carbonyl groups of the substrate; furthermore, if they do proceed by phosphorylation of the carbonyl group, the reaction may or may not proceed by way of monomeric metaphosphate. If, however, any of these reactions do proceed by attack of ATP on the carbonyl oxygen atom, with concommitant activation of the carbonyl group, the process would establish that ATP can play a kinetic as well as a thermodynamic role in intermediary metabolism.

Acknowledgment. This research was supported by the National Science Foundation Grant CHE 77-05948.

---

[12] Fullington, J. G.; Cordes, E. H. *J. Org. Chem.* **1964**, *29*, 970. Koehler, K.; Cordes, E. H. *J. Am. Chem. Soc.* 1970, *92*, 1576. Young, P. R.; Jencks, W. P. *Ibid.* **1977**, *99*, 8238. McClelland, R. A.; Ahmad, M. *Ibid.* **1978**, *100*, 7031.

[13] Guthrie, J. P. *J. Am. Chem. Soc.* **1973**, *95*, 6999; *Ibid.* **1974**, *96*, 588, 3608; *Can. J. Chem.* **1975**, *53*, 898. Satterthwait, A. C.; Jencks, W. P. *J. Am. Chem. Soc.* **1974**, *96*, 7018, 7031.

[14] Miller, D. L.; Westheimer, F. H. *J. Am. Chem. Soc.* **1966**, 1507, 1511, 1514. Miller, D. L.; Ukena, T. *Ibid.* **1969**, *91*, 3050. DiSabato, G.; Jencks, W. P. *Ibid.* **1961**, *83*, 4400. Benkovic, S. J.; Schray, K. J. *Biochemistry* **1968**, *7*, 4090. Haake, P.; Allen, G. *Proc. Natl. Acad. Sci. U.S.A.* **1971**, *68*, 2691; *J. Am. Chem. Soc.* **1973**, *95*, 8080; *Ibid.* **1976**, *98*, 4990.

[15] Levitski, A.; Koshland, D. E., Jr. *Biochemistry* **1971**, *10*, 3365.

[16] Mildvan, A. *Adv. Enzymol.* **1979**, *49*, 103. Knowles, J. R. *Annu. Rev. Biochem.*, in press. Spector, L. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 2626. Lowe, G.; Sproat, B. S. *J. Chem. Soc., Chem. Commun.* 1978, 783; *J. Chem. Soc., Perkin Trans. 1* 1978, 1622.

Tetraneopentyltitanium as a Polymerization Catalyst

James C. W. Chien,* Jiun-Chen Wu, and Marvin D. Rausch*

Contribution from the Department of Chemistry, Materials Research Laboratory, Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003.
Received March 10, 1980

Abstract: Tetraneopentyltitanium, (Neo)$_4$Ti, has been investigated as a polymerization catalyst. In the dark, it initiates slow homopolymerizations of styrene and methyl methacrylate, as well as their copolymerization. Reactivity ratios derived from copolymer compositions are in accord with a free radical process. The rates of polymerization of both monomers are greatly enhanced when they are irradiated with (Neo)$_4$Ti. The products in this case have a minor fraction like the polymers obtained in the dark, but in addition a major fraction of much lower molecular weight. Photolysis of (Neo)$_4$Ti produces trivalent titanium species as shown by EPR studies. However, the photolyzed products behave in the dark similarly to unphotolyzed (Neo)$_4$Ti in homo- and copolymerizations. (Neo)$_4$Ti under photolytic conditions also serves as a polymerization catalyst for ethylene and propylene. Mechanisms for these polymerization reactions are discussed.

Introduction

Homoleptic transition-metal σ-hydrocarbyls are often highly unstable; e.g., $TiMe_4$ decomposes readily even at low temperatures.[1] Stability can be enhanced by potential π-acceptor ligands, such as CO, PR_3, or η^5-$C_5H_5^-$. However, transition-metal-carbon σ bonds are not inherently weak; complexes can be made kinetically stable by means of ligands without β hydrogens such as the neopentyl group.[2-5] Even chemical inertness toward oxygen and protic reagents can be achieved with bulky bridgehead ligands such as norbornyl and camphyl,[6] which virtually fill the space

---

[1] K. Clauss and C. Beerman, *Angew. Chem.*, **71**, 627 (1959).

[2] W. Kruse, *J. Organomet. Chem.*, **42**, C39 (1972).

[3] P. J. Davidson, M. F. Lappert, and R. Pearce, *J. Organomet. Chem.*, **57**, 264 (1973).

[4] P. J. Davidson, M. F. Lappert, and R. Pearce, *Chem. Rev.*, **76**, 219 (1976).

[5] R. R. Schrock and G. W. Parshall, *Chem. Rev.*, **76**, 243 (1976).

0002-7863/81/1503-1180$01.25/0

surrounding the metal ion. The norbornyl compounds of first-row transition elements are thus kinetically stabilized in unusual coordination numbers, oxidation states, and electronic structures.[7,8]

Among the various interesting physical and chemical properties of β-elimination-stabilized transition-metal σ-hydrocarbyls is their ability to function as polymerization initiators. Tetranorbornylvanadium activated by diethylaluminum chloride or triethylaluminum has been used to homopolymerize and copolymerize ethylene and propylene.[9] $(Neo)_4Ti$ supported on silica and activated with diethylaluminum chloride also polymerizes ethylene.[10] Tetrabenzyltitanium, trisbenzyltitanium chloride, tetrakis(*p*-methylbenzyl)titanium, and tris(*p*-methylbenzyl)titanium chloride supported on Mg(OH)Cl and activated with aluminum alkyls have been used to polymerize ethylene as well as propylene.[11,12] In these instances, the catalysts presumably function in a manner proposed for Ziegler–Natta-type catalysts.

Furthermore, tetranorbornylmanganese can initiate vinyl polymerization in the presence of phenolic inhibitors.[13] Mintz and Rausch[14] have also shown that photolysis of $(Neo)_4Cr$ leads to polymerization of styrene, methyl acrylate, methyl methacrylate, and vinyl acetate as well as ethylene. The mechanism of polymerization of polar vinyl monomers by transition-metal σ-hydrocarbyls, with or without the assistance of light, is unclear, and the elucidation of this process is the central purpose of this study. The monomer pair selected for the investigation is styrene and methyl methacrylate because their reactivity ratios are known for free radical, anionic, and cationic copolymerizations.

Experimental Section

Materials. All operations were conducted under an argon atmosphere, using Schlenk tube techniques. Solvents were freshly distilled from calcium hydride under argon. $(Neo)_4Ti$ was prepared from neopentyllithium and titanium tetrachloride according to a published procedure.[3] The yellow solid gave a ^1H NMR spectrum identical with that reported in the literature[15] (CH_2, τ 7.64; CH_3, τ 8.62) with the correct integrated intensity ratio. The material was stored under argon at −20 °C in the dark. $(Neo)_4Cr$ was prepared as previously described.[2] Neopentane was prepared by the hydrolysis of neopentyllithium; 2,2,5,5-tetramethylhexane was obtained by refluxing neopentyl bromide and lithium in diethyl ether.[16] Styrene and methyl methacrylate were purchased from Polysciences, Inc. They were distilled before use and stored under argon at −20 °C in the dark.

Polymerization Procedures. In each case solid $(Neo)_4Ti$ or $(Neo)_4Cr$ was transferred to a Schlenk tube and weighed, and benzene was added to the desired concentration. The above solution (1.0 mL) was then introduced into 10.4 mL of monomer or comonomers. The final concentration of $(Neo)_4Ti$ or $(Neo)_4Cr$ was 5 mM. All polymerizations were carried out at 35 °C, except copolymerizations initiated by AIBN, which were done at 60 °C. The AIBN concentration was 12 mM and polymerization time was 1 h. Olefin polymerizations were carried out at 1 atm of monomer pressure, using 0.3 mmol of $(Neo)_4Ti$ in 30 mL of toluene at 35 °C. Homo- and copolymers were precipitated by the addition of methanol containing 1% hydrochloric acid.

Three methods of polymerization were employed. In method A, $(Neo)_4Ti$ together with the monomer or comonomers was irradiated with either a 275-W GE lamp or a 450-W medium-pressure Hanovia mercury lamp. In method B, a benzene solution of $(Neo)_4Ti$ was irradiated for 20 min and subsequently added to the monomer to initiate polymerization in the dark. Method C was simply polymerization in the dark. Controls were performed for all experiments omitting $(Neo)_4Ti$.

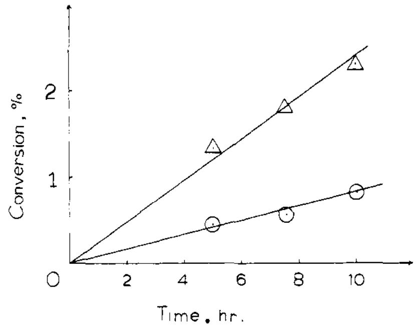


Figure 1. Rates of vinyl homopolymerizations in neat monomers at 35 °C: (⊙) styrene; (▲) methyl methacrylate. [$(Neo)_4Ti$] = 5 mM, total volume 11.4 mL, method C.

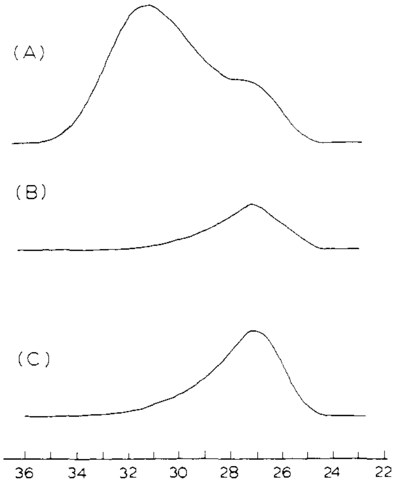


Figure 2, GPC curves for polysytrene initiated by $(Neo)_4Ti$: (A) by method A, 0.3% conversion; (B) by method B, 1.6% conversion; (C) by method C, 0.08% conversion.

Table I. Molecular Weights and Distributions of Homopolymers

method	% conversion	$\overline{M}_n$ PMMA	$\overline{M}_n$ PS	$\overline{M}_w/\overline{M}_n$ PMMA	$\overline{M}_w/\overline{M}_n$ PS
A	5.3	2.9×10^4, 7.0×10^5		1.8^a	
A	0.3		1.1×10^4, 8.2×10^4		2.0^a
B	1.2	3.8×10^5		2.3	
B	1.6		8.2×10^4		2.2
C	0.2	5.6×10^5		3.0	
C	0.08		1.0×10^5		2.5

[a] $\overline{M}_w/\overline{M}_n$ is that for the more abundant lower molecule weight products.

Characterization. The comonomer composition of the poly(styrene-*co*-methyl methacrylate) was determined by the 269-nm absorbance in the UV spectra,[17] obtained with a Cary 14 spectrometer, and from ^1H NMR spectra recorded with a Perkin-Elmer R-12A spectrometer. EPR spectra were obtained by means of a Varian E9 X-band spectrometer. Polymer molecular weights and polydispersities were determined with a Waters Associates GPC Model 200 instrument. A Varian Associates CFT 20 spectrometer was used to obtain ^{13}C NMR spectra of the homopolymers in order to determine the triad distribution.

Results

Homopolymerization. In the dark, $(Neo)_4Ti$ initiates slow polymerizations of methyl methacrylate and styrene. The rate of polymerization of 35 °C with 5 mM $(Neo)_4Ti$ is 6.3×10^{-6} M s^{-1} for methyl methacrylate; it is 2.0×10^{-6} for styrene (Figure

---

(6) B. K. Bower and H. G. Tennent, *J. Am. Chem. Soc.*, **94**, 251 (1972).

(7) G. A. Ward, B. K. Bower, M. Findlay, and J. C. W. Chien, *Inorg. Chem.*, **13**, 614 (1974).

(8) B. K. Bower, M. Findlay, and J. C. W. Chien, *Inorg. Chem.*, **13**, 759 (1974).

(9) W. P. Long, German Offen. 2204920.

(10) W. Kraus, German Offen. 2204927.

(11) J. C. W. Chien and J. T. T. Hsieh in "Coordination Polymerization", J. C. W. Chien, Ed., Academic Press, New York, 1975, pp 305–325.

(12) J. C. W. Chien and J. T. T. Hsieh, *J. Polym. Sci., Polym. Chem.*, **14**, 1915 (1976).

(13) J. C. W. Chien, unpublished results.

(14) E. A. Mintz and M. D. Rausch, *J. Organomet. Chem.*, **171**, 345 (1979).

(15) W. Mowat and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1120 (1973).

(16) S. H. Pine, B. A. Catto, and F. G. Yamagishi, *J. Org. Chem.*, **35**, 3663 (1970).

(17) A. V. Tobolsky, A. Eisenberg, and K. F. O'Driscoll, *Anal. Chem.*, **31**, 203 (1959).

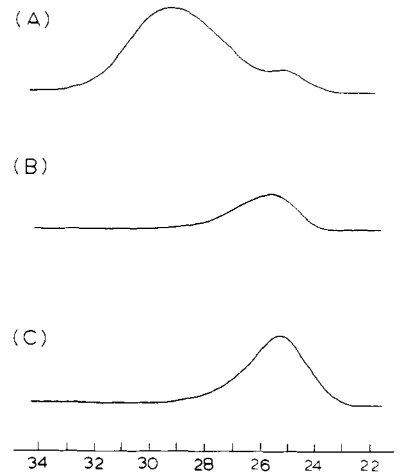


Figure 3. GPC curves for poly(methyl methacrylate) initiated by $(Neo)_4Ti$: (A) by method A, 5.3% conversion; (B) by method B, 1.2% conversion; (C) by method C, 0.2% conversion.

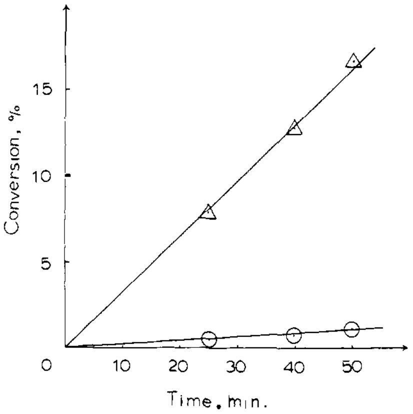


Figure 4. Rates of vinyl homopolymerizations. Legends are the same as in Figure 1. Polymerizations were by method A using a 450-W lamp.

1). The rates are relatively constant for low conversions. GPC analysis of polymers obtained after 15 min of polymerization gave the molecular weights and distributions summarized in Table I and Figures 2C and 3C.

Photolysis apparently accelerated the rate of polymerization, which is 5.2×10^{-4} and 2.9×10^{-5} M s^{-1} for methyl methacrylate and styrene (Figure 4), respectively. These homopolymers have bimodal distributions as shown in Figures 2A and 3A; the molecular weights are given in Table I for the polymer samples obtained after 15 min of photopolymerization.

If $(Neo)_4Ti$ was photolyzed under the same conditions as above but in the absence of monomer, subsequent homopolymerizations in the dark (method B) gave rates of 3.1×10^{-6} and 3.8×10^{-6} M s^{-1} for methyl methacrylate and styrene, respectively. Unlike the polymers obtained by method A, the polymers obtained by method B have monomodal molecular weight distribution and $\bar{M}_n$ values like those obtained by method C, as shown in Figures 2B and 3B.

The distributions of rr, mr, and mm triads in poly(methyl methacrylate) and polystyrene (Table II) were obtained from the α-methyl carbon[18] and the C_1 aromatic carbon resonances,[19] respectively.

Copolymerization. Copolymerizations of methyl methacrylate and styrene initiated by homolysis of AIBN at 60 °C were carried out for two purposes: (1) to provide samples for calibration of UV analysis of copolymer composition and (2) to ascertain under our experimental conditions the copolymer compositions for various comonomer feed ratios in free radical addition copolymerization. The copolymer compositions thus obtained are summarized in Table III. They gave copolymerization reactivity ratios in accord with those observed for free radical addition processes and very different from the values for either the anionic or cationic processes.[20]

In other copolymerizations a solution of $(Neo)_4Ti$ or $(Neo)_4Cr$ was added to the comonomer mixture and procedures A, B, and C were followed. The compositions of the copolymers obtained are summarized in Table III.

As in the homopolymerizations, the copolymers obtained under photolytic conditions are bimodal in molecular weight distributions

Table II. Microtacticity of Homopolymers

			triad %					
			aromatic C_1			α-methyl		
initiator	method	polymer	rr	mr	mm	rr	mr	mm
$(Neo)_4Ti$	A	PMMA				62	34	4
$(Neo)_4Ti$	A	PS	46	33	21			
$(Neo)_4Ti$	B	PMMA				65	33	2
$(Neo)_4Ti$	B	PS	58	27	15			
$(Neo)_4Ti$	C	PMMA				61	34	5
$(Neo)_4Ti$	C	PS	57	28	15			
$(Neo)_4Cr$	A	PMMA				60	37	3
$(Neo)_4Cr$	A	PS	50	31	19			

Table III. Composition of Styrene-Methyl Methacrylate Copolymers

	mol % of styrene in copolymer				
initiator:	AIBN	$(Neo)_4Ti$			$(Neo)_4Cr$
initiation method: mol % styrene in feed	thermal	A	B	C	A
18	27.5	26.5	28.0	27.5	27.5
32	39.0	38.0	39.5	39.0	38.0
53	54.0	53.0	53.0	53.0	52.0
70	66.2		66.2	66.2	67.5
80	73.5	73.0	73.0	73.2	72.3
88	81.0	82.3			
100	100	99.0			

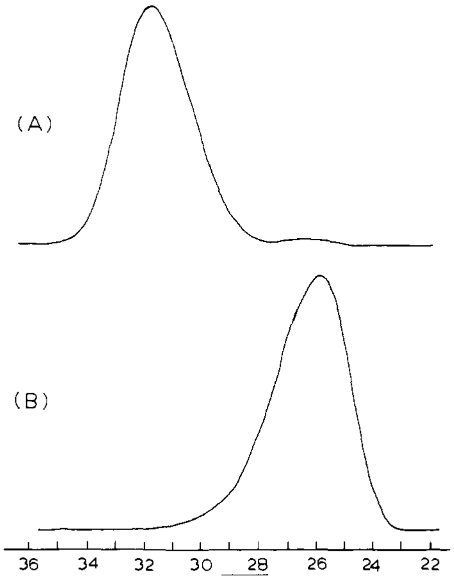


Figure 5. GPC curves for poly(styrene-*co*-methyl methacrylates) for 4:1 styrene: methyl methacrylate monomer feed ratio and initiated by $(Neo)_4Ti$: (A) by method A, 4.9% conversion; (B) by method B, 1.4% conversion.

---

(18) L. F. Johnson, F. Heatley, and F. A. Bovey, *Macromolecules*, **3**, 175 (1970).

(19) Y. Inoue, A. Nishioka, and R. Chujo, *Makromol. Chem.*, **156**, 207 (1972).

(20) Y. Lanler, *C. R. Hebd. Seances Acad. Sci.*, **230**, 539 (1950).

Table IV. Molecular Weights and Distributions of Styrene-Methyl Methacrylate Copolymers

	% styrene in comonomer feed					
	80		53		18	
method^a	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
A	9.2×10^3	1.6	1.2×10^4	1.9	1.8×10^4	1.7
A	2.6×10^5		5.6×10^5		5.6×10^5	
B	2.6×10^5	2.5	1.8×10^5	2.5	1.2×10^5	1.9

^{a} Polymerization initiated by $(Neo)_4Ti$.

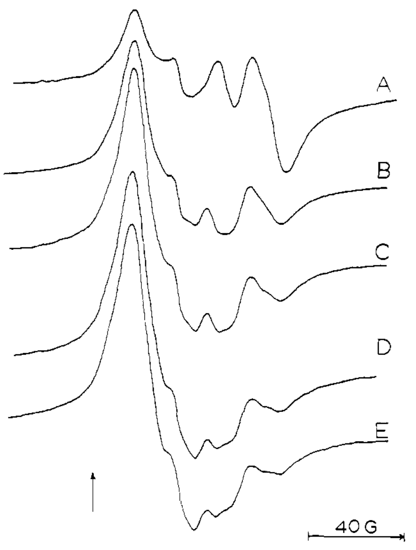


Figure 6. EPR spectra of irradiated benzene solution of $(Neo)_4Ti$. Length of irradiation: (A) 1 min; (B) 5 min; (C) 10 min; (D) 30 min; (E) 40 min. Spectrum A has twice the instrument gain. Marker is for DPPH.

even though the high $\overline{M}_n$ fraction is very small, whereas those polymerized in the dark are monomodal. The results are given in Table IV and Figure 5, assuming the applicability of the universal calibration curve.

Olefin Polymerizations. Olefin polymerizations were carried out with $(Neo)_4Ti$ at 35 °C under photolysis conditions. At 1 atm of ethylene pressure, 0.22 g of polyethylene was obtained after 4 h of photolysis. Under the same conditions, propylene polymerizes to give 0.06 g of polypropylene. No polymer was obtained with either monomer when there was no irradiation. If $(Neo)_4Ti$ was irradiated for 20 min and then ethylene was introduced, 4 h of reaction in the dark yielded 0.07 g of polyethylene.

Photolysis of $(Neo)_4Ti$. Irradiation of a light yellow solution of $(Neo)_4Ti$ in benzene, toluene, or hexafluorobenzene caused immediate photodecomposition to give a black solution containing a black precipitate. The vapor phase was sampled, and a comparison with an authentic sample by GC showed the major photolysis product to be neopentane. Small aliquots of the solution were also analyzed by GC and found to contain 2,2,5,5-tetramethylhexane when compared with an authentic sample.

Electron paramagnetic resonance (EPR) was used to follow the appearance of trivalent titanium species formed by photolysis of a benzene solution of $(Neo)_4Ti$. Figure 6 shows the EPR spectra as a function of irradiation time. Even 1 min of irradiation produces an intense EPR spectrum containing four Ti(III) species, I, II, III, and IV, with g values of 1.988, 1.982, 1.973, and 1.963, respectively. Increasing the period of illumination has only a small effect on species II, III, and IV but enhances the signal of species I (Figure 7). Species IV reaches stationary concentration almost immediately, whereas it takes about 30 min of irradiation for species I to reach the same (Figure 7). The concentration of species III decreases with irradiation. It is also thermally unstable since, upon standing following photolysis, it decreases in intensity whereas the other resonances remain unchanged. The effect of temperature on the EPR spectra is illustrated in Figure 8.

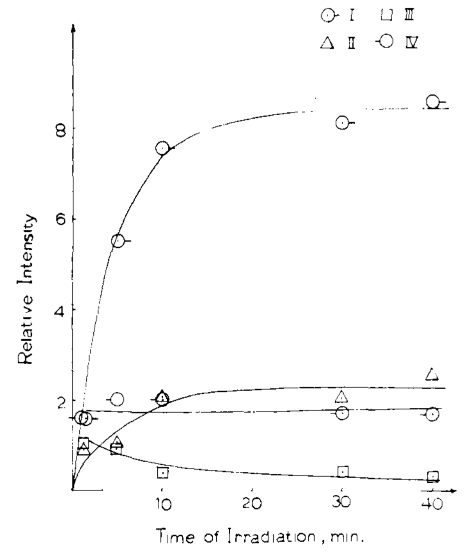


Figure 7. Change in EPR signal intensity for g values: (⊙-) 1.988; (▲) 1.982; (⊡) 1.973; (-⊙) 1.963.

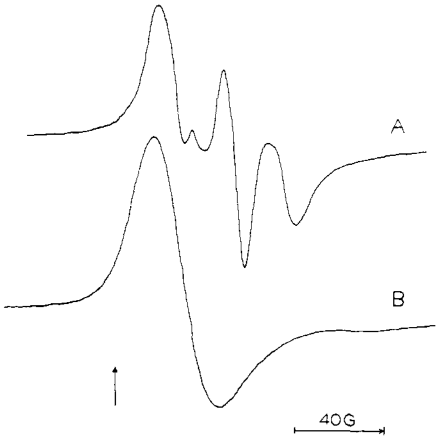


Figure 8. EPR spectra of $(Neo)_4Ti$ in benzene after 1 min of irradiation: (A) 25 °C, receiver gain 400×; (B) −195 °C, receiver gain 100. Marker is for DPPH.

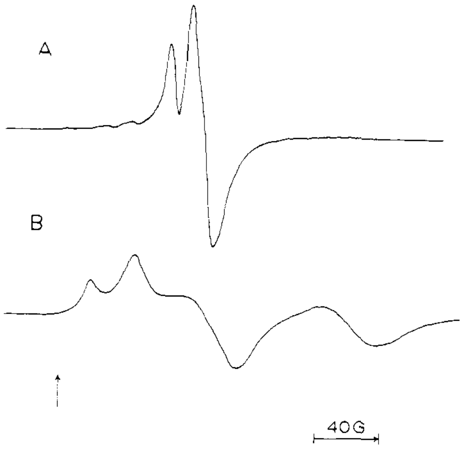


Figure 9. EPR spectra of Ti(III) species formed by the irradiation of $(Neo)_4Ti$ in neat methyl methacrylate after 50 min of irradiation: (A) 25 °C; (B) −195 °C. Marker is for DPPH.

Photolysis of $(Neo)_4Ti$ in the presence of monomer gave Ti(III) products which are markedly different from the above. Figure 9A is the EPR spectrum of $(Neo)_4Ti$ irradiated in neat methyl methacrylate. There are clearly two major Ti(III) species produced, with g_{iso} values of 1.952 and 1.964. Both species increase monotonically with the length of irradiation. At −195 °C (Figure 9B) the EPR spectrum showed the two Ti(III) products to be

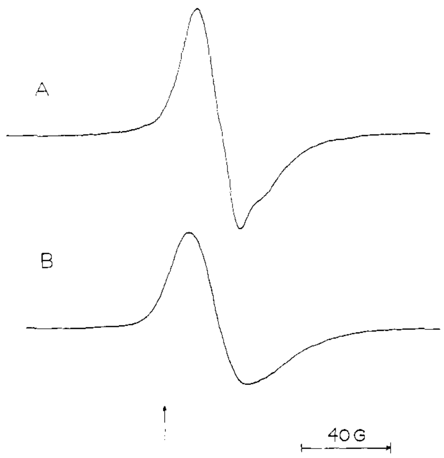


Figure 10. EPR spectra of Ti(III) species formed by the irradiation of $(Neo)_4Ti$ in neat styrene after 50 min of irradiation: (A) 25 °C; (B) −195 °C.

strongly anisotropic. The $g_{iso} = 1.952$ species has $g_{\parallel} = 1.978$ and $g_{\perp} = 1.903$, whereas the $g_{iso} = 1.964$ species has $g_{\parallel} = 1.992$ and $g_{\perp} = 1.950$. Irradiation of $(Neo)_4Ti$ in neat styrene produces a single Ti(III) product with a nearly isotropic g value of 1.990 (Figure 10A). At liquid nitrogen temperature, the spectrum (Figure 10B) does not show increased anisotropy. As in the previous case, the concentration of this paramagnetic species also increases with the length of irradiation.

$(Neo)_4Ti$ solution in the dark, with or without monomer, does not develop an EPR spectrum.

Discussion

Photopolymerization. That photolysis of transition-metal alkyls can lead to homolysis is well documented. Radical products were observed in the photolyses of $(\eta^5\text{-}C_5H_5)_2MMe_2$ (M = Ti, Zr, Hf),[21,22] $(\eta^5\text{-}C_5H_5)_2TiPh_2$,[23] and various organocobalt complexes.[24] Irradiation of $PhCH_2Mn(CO)_5$ in the presence of the spin trap nitrosodurene has led to the EPR identification of the nitroxides derived from both $PhCH_2$ and $Mn(CO)_5$.[25] M–C homolysis has been reviewed in the context of free radical organometallic chemistry..[26] In the case of homoleptic transition-metal σ-hydrocarbyls such as $(Nor)_4M$ (M = Ti, Mn, Co, Fe, V), their photolysis afforded a mixture of norbornane and 1,1-binorbornyl in quantitative yields.[6] Photolysis of $CpPtMe_3$ in the absence of a spin trap led to unequivocal EPR identification of matrix-isolated methyl radical.[27]

Vinyl polymerizations were initiated by the photolysis of $(\eta^5\text{-}C_5H_5)_2TiMe_2$.[28] Ballard and van Lienden had reported the polymerization of vinyl monomers by tetrabenzylzirconium (Bz_4Zr) with[29] and without[30] irradiation. Their results superficially resemble our findings but the two systems show significant differences as will be discussed below.

The photolysis of $(Neo)_4Ti$ most certainly leads to homolysis (eq 1). The expected products from the neopentyl radical,

$$(Neo)_4Ti \xrightarrow{h\nu} (Neo)_3Ti + Neo \qquad (1)$$

neopentane and 2,2,5,5-tetramethylhexane, were both found, as well as the EPR signals for trivalent titanium complexes.

Two potential initiators are produced in the photolysis; their ability to initiate polymerization depends upon the monomer. In this and previous work[14] of polymerizations of olefins initiated by photolyses of homoleptic Ti and Cr σ-hydrocarbyls, semicrystalline polyethylenes and polypropylenes were obtained. These monomers do not undergo free radical addition polymerizations under these conditions. Undoubtedly, in these cases some Ti(III) species act as catalysts of the Ziegler–Natta type. Also, some ethylene polymerization occurred with procedure B, where free radicals are absent.

In the case of styrene and methyl methacrylate, photoinitiation produces homopolymers with bimodal distributions, indicating that two different propagation mechanisms are operative. The low molecular weight fractions are produced in larger quantities; 72% of the total for polystyrene and 88% for poly(methyl methacrylate). They have $\bar{M}_w/\bar{M}_n$ ratios very close to 2 (Table I). The compositions of the copolymers obtained with method A and AIBN thermal initiation are identical over the entire range of comonomer feed ratios (Table III). Furthermore, Ballard and van Lienden[30] in their studies found that the rate of styrene polymerization initiated by light of 300–450 nm is proportional to the square root of the light intensity. All these results are consistent with a simple free radical addition mechanism. The difference between Ballard's work and ours is that $(Bz)_4Zr$ produced polymers with $\bar{M}_w/\bar{M}_n = 4.45$. This result may be due to the fact that the molecular weights of their polystyrene were much lower and some portions were not precipitated in the workup.

The minor fraction of homo- and copolymers in method A is produced in rates and molecular weights comparable to those obtained by methods B and C. It is reasonable to assume that they share the same polymerization mechanism.

Dark Polymerization. There are some interesting features in the polymers obtained by methods B and C. The compositions of poly(styrene-*co*-methyl methacrylate) produced by these methods are the same as those polymerized with AIBN. Also the microtacticity of poly(methyl methacrylate) is indistinguishable between products obtained with methods A, B, and C. However, the microtacticity of polystyrene obtained with procedures B and C differs somewhat from that of the photoinitiated products.

If the dark polymerization is initiated by free radicals, it may be the result of homolysis. Such a process has been thought to be unimportant for homoleptic Ti and Cr σ-hydrocarbyls.[26] In our studies, the possibility that the dark polymerization is the ordinary free radical process may be discounted. First, only monomodal polymers should result from procedure A if both the photopolymerizations and dark polymerizations proceed via a free radical addition mechanism. Suppose that free radicals are formed by both photolysis and thermolysis to cause initiations of rate R_i^p and R_i^d, respectively; then the overall rate of polymerization is simply

$$R_p = k_p[M][(R_i^p + R_i^d)/2k_t]^{1/2} \qquad (2)$$

and a molecular weight of

$$\bar{M}_n = k_p M_0 [M][2(R_i^p + R_i^d)k_t]^{-1/2} \qquad (3)$$

is attained. k_p and k_t are the rate constants of propagation and termination, respectively. If $R_i^p \gg R_i^d$, as is the case, then both R_p and $\bar{M}_n$ are largely determined by the photochemical process. In eq 3 M_0 and [M] are the molecular weight and concentration of the monomer, respectively. In any event, no bimodal distribution would be expected.

Secondly, the molecular weights of the homopolymers produced in the dark are not consistent with the observed polymerization rate for a free radical mechanism. At 35 °C the rate constants have been reported to be $k_p = 280\ M^{-1}\ s^{-1}$ and $k_t = 2 \times 10^7\ M^{-1}\ s^{-1}$ for methyl methacrylate polymerization and $k_p = 125\ M^{-1}\ s^{-1}$ and $k_t = 1.22 \times 10^8\ M^{-1}\ s^{-1}$ for styrene in free radical processes.[31]

---

[21] M. D. Rausch, W. H. Boon, and H. G. Alt, *J. Organomet. Chem.*, **141**, 299 (1977).

[22] E. Samuel, P. Maillard, and C. Giannotti, *J. Organomet. Chem.*, **142**, 289 (1977).

[23] M. D. Rausch, W. H. Boon, and E. A. Mintz, *J. Organomet. Chem.*, **160**, 81 (1978).

[24] J. M. Pratt and B. R. D. Whitear, *J. Chem. Soc. A*, 253 (1971).

[25] A. Hudson, M. F. Lappert, P. W. Lednor, and B. K. Nicholson, *J. Chem. Soc., Chem. Commun.*, 966 (1974).

[26] M. F. Lappert and P. W. Lednor, *Adv. Organomet. Chem.*, **14**, 345 (1976).

[27] O. Hackelberg and A. Wojlcicki, *Inorg. Chim. Acta*, **44**, 663 (1980).

[28] C. M. Bamford, R. J. Puddephatt, and D. M. Slater, *J. Organomet. Chem.*, **159**, 631 (1978).

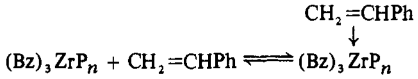
[29] D. G. H. Ballard and P. W. van Lienden, *Makromol. Chem.*, **154**, 177 (1972).

[30] D. G. H. Ballard, J. V. Dawkins, J. M. Key, and P. W. van Lienden, *Makromol. Chem.*, **165**, 173 (1973).

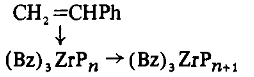
[31] H. G. Elias, "Macromolecules", Vol. 2, Plenum Press, New York, 1977, p 710.

Substituting these values into eq 2 and 3 gives $\bar{M}_n$ of several million. The homopolymers obtained with $(Neo)_4Ti$ have much smaller molecular weights.

Dark polymerizations initiated by $(Bz)_4Zr$[30] have none of the features of free radical reactions. Ethylene was polymerized at low pressure and styrene and methyl methacrylate were copolymerized to products having a composition differing significantly from that obtained with known radical system. However, neither a description of copolymerizations nor the actual composition of copolymer was given. The authors proposed a coordinated anionic mechanism with the tetravalent zirconium complex as the active species. Approximately 0.1% of the $(Bz)_4Zr$ is active at any given time; this is attributed to equilibrium 4 lying far to the left, where P_n represents a polymer moiety. In contrast $(Neo)_4Ti$ does not polymerize ethylene in the dark, and it produces poly(styrene-*co*-methyl methacrylate) with free radical reactivity ratios.



$$(Bz)_3ZrP_n + CH_2{=}CHPh \rightleftharpoons \overset{CH_2=CHPh\ \downarrow}{(Bz)_3ZrP_n} \quad (4)$$



$$\overset{CH_2=CHPh\ \downarrow}{(Bz)_3ZrP_n} \rightarrow (Bz)_3ZrP_{n+1} \quad (5)$$

A coordinated-radical mechanism would be consistent with the polymerization results described above. The propagating species is proposed to be a caged radical

$$(Neo)_3TiP_n \rightleftharpoons [(Neo)_3Ti + P_n\cdot] \quad (6)$$

$$[(Neo)_3Ti + P_n\cdot] + M \rightarrow [(Neo)_3Ti + P_{n+1}\cdot] \quad (7)$$

$$[(Neo)_3Ti + P_{n+1}\cdot] \rightleftharpoons [(Neo)_3TiP_{n+1}] \quad (8)$$

where M is the monomer. Cage escape could lead to some free radical reactions. It is unlikely that a Ti(II) complex will be the active species, since it tends to reduce intramolecularly the polymer moiety to $P_n(-H)$.

A number of termination processes may be possible. β-Hydrogen elimination can provide a chain-transfer pathway

$$(Neo)_3TiP_n \rightarrow (Neo)_3TiH + P_n(-H) \quad (9)$$

Radicals which escape the cage could cause termination

$$(Neo)_3TiP_n + P_m\cdot \rightarrow (Neo)_3Ti + P_n(+H) + P_m(-H)\ (\text{or } P_{n+m}) \quad (10)$$

A less probable process because of steric reasons is

$$(Neo)_3TiP_n + (Neo)_4Ti \rightarrow (Neo)_3T_i{-}CH_2{-}C(Me)_2{-}T_i(Neo)_3 + P_n(+H) \quad (11)$$

This is binuclear elimination without concomitant change in metal oxidation state.[3] A 1,2-elimination can also be considered

$$(Neo)_3TiP_n \rightarrow (Neo)_2Ti{=}CHCMe_3 + P_n(+H) \quad (12)$$

Both reactions 11 and 12 have been proposed[3,32] for the decomposition of $TiMe_4$.

An observation which tends to support the coordinated-radical mechanism is the effect of radical scavengers. Dark polymerization (methods B and C) have increased rates when diphenylpicrylhydrazyl was present. DPPH probably scavenges the free radical which had escaped the cage; consequently the occurence of the most probable termination reaction 10 is reduced.

EPR Spectra. The EPR spectra of Ti(III) species produced by the photolysis of $(Neo)_4Ti$ are markedly different, depending upon whether the medium is benzene, styrene, or methyl methacrylate. Such dependence has been noted elsewhere. For instance, the zero-field splitting of $(Nor)_4Cr$ was found[7] to be sensitive to the solvent and temperature.

Photolysis of $(Neo)_4Ti$ in benzene produces an EPR spectrum containing four signals (Figure 6). Cooling the sample to −195 °C causes the four signals to coalesce into a single one. These changes are reversible. It is likely that the signals with different *g* values reflect the ligand field splittings of the Ti(III) species. For instance, they may be $(Neo)_3Ti$ having different numbers of benzene molecules loosely coordinated in different orientations, i.e., edgewise or face-on. They all convert to the most stable species at −195 °C.

In contrast, the EPR signal formed by the photolysis of $(Neo)_4Ti$ in neat styrene shows predominantly one *g* value with a hint of a shoulder on the high-field side (Figure 10). The liquid nitrogen temperature spectrum is about the same as it is at room temperature. Either styrene does not coordinate with $(Neo)_3Ti$ or there is only one complexed form.

The converse is true when $(Neo)_4Ti$ is photolyzed in neat methyl methacrylate. Figure 9 shows a room-temperature EPR spectrum with two *g* values. The −195 °C spectrum has four *g* values. It is likely that there are two different monomer-coordinated Ti(III) species, each with large *g* anisotropies.

Acknowledgment. We are grateful to the National Science Foundation for a grant to MDR and to the Exxon Research and Development Co. for a grant to J.C.W.C. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

---

(32) F. S. D'yachkovskii and N. E. Khruschch, *J. Gen. Chem. USSR (Engl. Transl.)*, **41**, 1787 (1971).