

Interference between Reactants in Simultaneous Interpenetrating Polymer Network Formation. II. Influence of the Presence of a Free-Radical Initiator on Polyurethane Formation

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ABSTRACT: Polyether polyurethane networks were prepared in solution at 25 and 60°C, using various organotin catalysts. The presence of a free-radical initiator [viz. azobisisobutyronitrile (AIBN)] in the reaction media has no effect on the catalytic efficiency of organotin(IV) compounds, whereas it causes severe deactivation of organotin(II) compounds. This effect was explained by the following mechanism: formation of a cyclic 1 : 1 complex by coordination of the nitrile groups of AIBN with the tin(II) atom, which both reduces the effective catalyst concentration and allows the early decomposition into radicals, as previously seen, leading to tin oxidation. The addition of a free-radical scavenger such as 3-*tert*-butyl pyrocatechol allows the maintenance of the catalyst efficiency of organotin(II) compounds at their reference level. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1929–1937, 2002

Key words: polyurethane networks; organotin catalyst; free-radical initiator; coordination complex

INTRODUCTION

This work was undertaken as part of our current studies on the synthesis and characterization of interpenetrating polymer networks (IPNs).^{1–4} Simultaneous polyurethane/poly(methyl methacrylate) (PUR/PMMA) IPNs have attracted special attention, and relations between conditions of network formation and properties of the end materials were investigated.^{5–8} Extensive kinetic studies by Fourier transform infrared spectroscopy^{7,8} have shown the following two phenomena: (1) the rate of free-radical polymerization and

crosslinking of methyl methacrylate is faster in the presence of stannous octoate (SnOc_2), which is the catalyst of the polyurethane step polymerization; and (2) the formation of the polyurethane network is slowed down and even incomplete because of the decomposition into radicals of azobisisobutyronitrile (AIBN) at low catalyst concentration over free-radical initiator concentration ratios $[\text{SnOc}_2]/[\text{AIBN}]$. The first phenomenon was already explained and published.⁹ Kinetic measurements of PMMA formation in solution have revealed the synergistic role of SnOc_2 , which only concerns the initiation rate of polymerization, and the results were explained by assuming the formation of a cyclic complex between the nitrile groups of AIBN and the tin(II) atom of SnOc_2 . Unfortunately, we did not succeed in isolating

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that complex. Also, the formation of a cyclic 1 : 1 complex between AIBN and SnOc_2 was confirmed by the increase in the rate of thermal decomposition of AIBN in the presence of SnOc_2 due to steric constraints in the azo links of the complexed initiator.¹⁰

This article will focus on the second phenomenon previously observed, namely, the inhibition effect of AIBN on the catalytic activity of stannous octoate for the isocyanate–alcohol reaction.

It is well known that similar to tertiary amines, organometallic compounds are commonly used in the manufacture of polyurethanes.^{11,12} Organotin compounds are among the most effective catalysts because they promote reaction of isocyanate with hydroxyl groups in preference to reaction with water.¹³ Several mechanisms were proposed but the actual reaction mechanism is still uncertain in spite of numerous investigations.^{14–17} It is assumed that the reaction proceeds with the formation of intermediate complexes.^{18,19} The complex formation could occur in two steps with the first activation of the hydroxyl group and the formation of a ternary complex with the isocyanate function by coordination with the oxygen atom and nitrogen atom as well, thus increasing the electrophilic nature of the isocyanate function. Urethane formation would then take place by proton rearrangement. Activation of isocyanate–alcohol reactions comes from the donor–acceptor complex-forming ability of tin, having free 5 d orbitals in the low-energy level. The rate of urethane formation is further determined by the rate of dissociation of the labile complexes. Thus, the efficiency of the catalysts would be very dependent upon the stability of these complexes, which, in turn, would be determined by the nature of the substituents, the configuration, and the electronic structure of the coordination complex.^{12,20} On the other hand, organometallic compounds of electron-deficient metals (i.e., Co, Ni, Sn, and Pb) may form more or less stable complexes with oxygen and nitrogen donor ligands.^{21–23} In some rare cases, these complexes were isolated and structurally characterized. The number of divalent tin complexes is very low compared to tetravalent tin complexes. From a literature survey,^{24,25} it appears, to date, that tin(IV) complexes have mostly a 1 : 2 Sn : ligand molar ratio, whereas tin(II) complexes exhibit various compositions. This large variety of structure for divalent tin complexes could be ascribed to their low stability.

Organometallic compounds are known to react with radicals^{26,27} according to various mecha-

nisms such as atom transfer, electron transfer, fragmentation, substitution, or oxidation. Thus, under some conditions, the catalytic activity of organotin compounds, such as SnOc_2 or dibutyltin dilaurate (DBTDL), is reduced, inducing lower polymerization rates. According to various authors,^{19,23,28–30} retarding effects are explained by stabilization of the tin compounds and complexation with carboxylic acids,^{19,29} benzyl alcohol,²³ and ester groups.³⁰ Even entire deactivation of dibutyltin diacetate (DBTDA) by protons was reported by Van der Weij.¹⁹ Finally, He et al.³¹ have observed a strong inhibition effect on the crosslinking reaction of dihydroxy polydimethylsiloxane catalyzed by SnOc_2 due to the presence of radicals and oxygen.

In addition to the previous studies^{9,10} on interaction between SnOc_2 and AIBN, we have studied tin-catalyzed polyaddition reactions of isocyanate with macrodiol in solution in the presence of various amounts of AIBN, or mixtures of AIBN and a free-radical scavenger. Experiments were made at 60 and 25°C, which are temperatures at which AIBN does or does not decompose into radicals, respectively. Ethyl acetate was the solvent and was used at the same concentration (66 wt %) as was methyl methacrylate for the synthesis of simultaneous IPNs.⁸

EXPERIMENTAL

Materials

Polypropylene oxide (Arcol 1020) from Arco Chemical had an average molar mass close to 2000 g/mol, corresponding to an OH number of 55 mgKOH/g. This macrodiol was dried by keeping it over activated 4-Å molecular sieves, but not otherwise purified. The pluriisocyanate was an adduct of toluene diisocyanate (TDI) and trimethylol propane, kindly supplied by Bayer under the trade name Desmodur L-75 in the form of a 75% solution in ethyl acetate. This product was used without further purification. Its equivalent weight was determined as 3.06 mEq/g by using classical dibutylamine titration. The organotin compounds used were stabilized³² stannous octoate (SnOc_2) (Kosmos 29 from Goldschmidt), DBTDL (Kosmos 19 from Goldschmidt), and dibutyltin bis(2-ethyl hexanoate) (DBTEH) from Alfa Johnson Matthey. They contained 29.3, 18.5, and 22.9% tin by weight, respectively. Not otherwise purified, they were stored under nitrogen at a low temperature until use. AIBN (Merck) was recryst-

Table I Time to Gel for the Macrodiol-Pluriisocyanate Reaction in Solution Using Various Tin Catalysts and Weight Equilibrium Swelling Degree in Ethyl Acetate of the Polyurethane Networks thus Obtained

Catalyst	Amount (wt %)	Gelation at 25°C (min)	Gelation at 60°C (min)	Q_w
DBTDL	0.1	600	70	—
DBTEH	0.1	600	70	—
SnOc ₂	0.1	50	5	5.3
oSnOc ₂ ^a	0.1	150	12	—
DBTDL	1.0	300	27	5.3
DBTEH	1.0	420	30	5.8
SnOc ₂	1.0	15	4	5.0
oSnO ₂ ^a	1.0	25	5	—

^a Oxidized stannous octoate.

tallized from methanol before use. 4-*Tert*-butylpyrocatechol (TBPC) was used as received from Merck. Its purity was better than 98%. Ethyl acetate (Merck) was analytical grade and only dried over activated 4-Å molecular sieves before use as solvent.

Procedure

Polyurethane networks were prepared in solution by using a one-step procedure that consists of the end-linking of the OH groups of the polypropylene oxide chains by the NCO groups of the pluriisocyanate. A typical procedure is as follows. In a reaction flask equipped with nitrogen inlet and a magnetic stirrer and placed in a water bath, 1 mol macrodiol is mixed with 1.07 mol pluriisocyanate ($k = [\text{NCO}]/[\text{OH}] = 1.07$)³³ and dissolved in ethyl acetate to form a 34 wt % homogeneous solution. When appropriate, calculated amounts of AIBN and TBPC were added to the solution under stirring. The catalyst (i.e., the organotin compound) was last introduced with a syringe. This moment was considered as the origin of the reaction. The polyurethane-forming reaction was carried out at 25 and 60°C for about 3 h.

Methods

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 60SX spectrophotometer equipped with a Specac heating chamber, using NaCl cells. The number of scans was 32 for 1 min and the resolution was 2 cm⁻¹. The progress of the reaction was monitored by following the decrease of the normalized absorbance of the characteristic NCO peak at 2275 cm⁻¹. The peak located at 2950 cm⁻¹ corresponding to the CH₂

stretching was taken as internal standard. Gelation was determined in an empirical way: the reactive mixture was placed in a closed glass tube (~ 10 mL) immersed in a water bath. At regular intervals, the tube was removed from the bath and inverted to observe the flow behavior of the solution. The time at which the solution ceased to flow was taken as the gel point. Because of the abrupt change in viscosity, reproducibility of the gel time was within 1 min. For swelling experiments, performed at room temperature, small samples of polyurethane networks were immersed in excess ethyl acetate and allowed to swell to equilibrium in approximately 10 days. During swelling, the solvent was renewed twice. The swollen samples were removed from the liquid, surface dried with filter paper, and rapidly weighed. The absorbed ethyl acetate was then completely evaporated under vacuum, and the samples reweighed. The equilibrium swelling degree, Q_w , is the ratio of the weights of network in the swollen state and the dry state. Measurements were repeated for three different samples of each network, and the results were averaged.

RESULTS AND DISCUSSION

Influence of the Type of Catalyst on Gelation

Divalent and tetravalent organotin compounds were used as catalyst for the formation of polyurethane networks in ethyl acetate. Two levels of catalyst, 0.1 and 1.0 wt %, were taken, and the polyaddition was conducted at two different temperatures. Time to reach the gel point is reported in Table I. It appears that tin valency has a strong

Table II Time to Gel (in min) of the Macrodiol-Pluriisocyanate Reaction in Ethyl Acetate Catalyzed by the SnOc₂-AIBN Pair with Various Relative Concentrations at 25 and 60°C

Temperature	25°C	25°C	25°C	60°C	60°C	60°C
SnOc ₂ (%)	1.0	0.2	0.1	1.0	0.2	0.1
AIBN (%)						
0	15	45	50	4	4	5
0.05	—	—	No gel	—	—	30
0.1	19	60	No gel	5	12	No gel
0.2	—	1200	—	—	140	—
0.3	23	No gel	—	5	—	—
0.5	31	—	No gel	5	480	No gel
1.0	40	No gel	No gel	6	No gel	No gel

influence on gelation of polyurethane: the tin(II) compound allows a much faster isocyanate-alcohol reaction than tin(IV) compounds. The difference in catalytic activity is particularly emphasized at room temperature, using low amounts of catalyst. The steric hindrance of tin derivative is also an important parameter¹¹ to consider for evaluation of its catalytic activity: DBTEH with an ethyl group in α position of the carbonyl group is less active than DBTDL whose main chain is linear.

Previous studies³² have shown that SnOc₂ is very sensitive to oxidation. It is the reason the commercial product is stabilized and kept at low temperature. To verify the effect of oxygen on the catalytic activity of SnOc₂, a small amount of the divalent tin derivative was exposed to air for 24 h at room temperature prior to its use as the catalyst. When taken 1 wt %, gelation of polyurethane occurs approximately at the same time as if fresh SnOc₂ was used. The relatively high amount of catalyst could mask an eventual modification of catalytic activity. However, at low concentration, the effect of oxygen poisoning is much clearer: gelation is approximately reduced three times.

Geometry and valency of the studied organotin compounds, and the time to gel, seem to have no effect on the equilibrium swelling degree of the final polyurethane network: whatever the catalyst, the equilibrium swelling degree has a value of 5.4 ± 0.4 (see Table I), which means that the various polyurethane networks have almost same structure.

Influence of the SnOc₂-AIBN Pair on Polyurethane Gelation

Various amounts of SnOc₂ and AIBN were used as the catalytic system for the macrodiol-pluri-

isocyanate reaction performed in the same experimental conditions as previously, namely, in ethyl acetate solution, and at two different temperatures (25 and 60°C). Gel times are reported in Table II. At 60°C, for 1.0% SnOc₂, the crosslinking reaction is not very sensitive to the presence of radicals formed by the decomposition of AIBN at that temperature (Fig. 1). However, at 25°C, gel time increases with the concentration of AIBN but a gel is always obtained within reasonable time, whatever the amount of AIBN, in the range of 1.0–0.5% SnOc₂. For lower concentrations, gelation depends on the relative amounts of SnOc₂ and AIBN. For instance, at room temperature, with 0.3% SnOc₂ and 0.5% AIBN, the gel time exceeds 7 h, whereas gelation is already obtained after 28 min in the absence of AIBN.

For concentrations of 0.2 and 0.1% SnOc₂, gelation becomes more and more difficult, and even

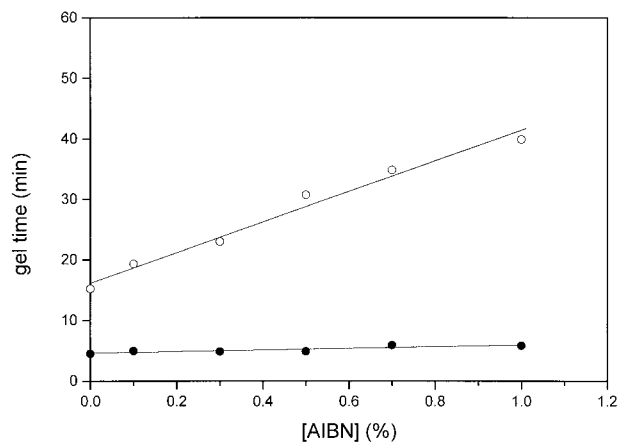


Figure 1 Gelation of the catalyzed macrodiol-pluriisocyanate reaction in the presence of various amounts of AIBN. [SnOc₂] = 1%. Temperatures: (○) 25°C; (●) 60°C.

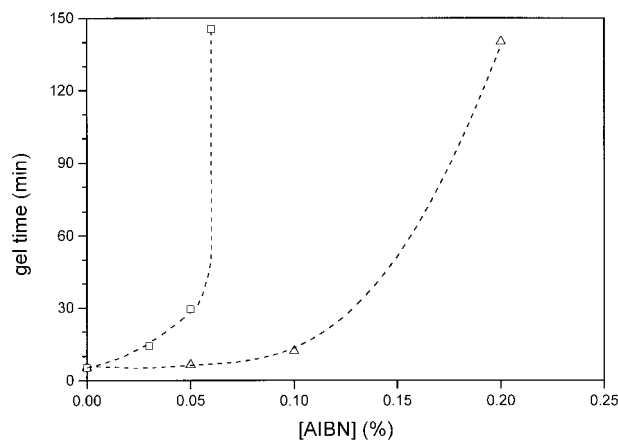


Figure 2 Gelation of the catalyzed macrodiol-pluriisocyanate reaction in the presence of various amounts of AIBN at 60°C. $[\text{SnOc}_2] = (\square) 0.1\%$; $(\triangle) 0.2\%$.

impossible, in the presence of increasing amounts of AIBN (Table II). This clearly appears in Figure 2. For the SnOc_2 -AIBN pair, there is a critical concentration of AIBN which causes the stop of the crosslinking reaction. This value strongly depends on temperature: the presence of 0.3% AIBN at 25°C, or 0.6% AIBN at 60°C, inhibits the catalytic activity of 0.2% SnOc_2 . When using only 0.1% organotin(II) compound, gelation is still possible at 60°C in the case of AIBN concentrations equal to or lower than 0.05%. Despite the number of compositions of the SnOc_2 -AIBN pairs examined, no correlation was found between weight or molar ratio, temperature, and complete inhibition of the polyaddition.

Using organotin(IV) compounds such as DBTDL or DBTEH instead of SnOc_2 , the presence of AIBN, even in very high concentrations, does not modify formation and gelation of polyurethane at 25 or 60°C (Table III). Gel times are of the same order of magnitude and to a first approach, inhibition previously observed for SnOc_2 is not observed for tetravalent tin catalysts.

Influence of the Presence of AIBN on Equilibrium Swelling Degree of Polyurethane Networks

The equilibrium swelling degrees in ethyl acetate determined for polyurethane networks prepared at 25°C as well as at 60°C confirm the conclusions previously drawn from gel time data. Using AIBN concentrations lower than the critical concentration, the equilibrium swelling degree of SnOc_2 -catalyzed polyurethane networks is identical to Q_w of networks obtained in the absence of AIBN (i.e., 5.4 ± 0.4). Using AIBN with higher concen-

trations, Q_w increases drastically, indicating the presence of defects in the network structure due to incomplete reaction. Concerning networks obtained using organotin(IV) compounds such as DBTDL or DBTEH, their equilibrium swelling degree is not sensitive to the presence of AIBN and is found to be identical to that of classical SnOc_2 -catalyzed networks, made in the absence of AIBN. Once again, one can conclude that AIBN does not interact with tetravalent tin compounds and that the presence of AIBN in the reaction medium does not modify under any circumstances the mechanism of tin(IV)-catalyzed polyaddition, because the final materials seem to be identical whatever the experimental conditions.

Influence of the Presence of AIBN on the Consumption of NCO Groups

To better understand the inhibition phenomenon of SnOc_2 by AIBN, the conversion of the isocyanate group during formation of the polyurethane network was followed by FTIR. Conversion versus reaction time appears in Figure 3 for SnOc_2 -catalyzed reactions at 60°C, in the presence and in the absence of radicals originating from the decomposition of AIBN at that temperature. It can be seen that even with a high amount of AIBN, the polyaddition is initiated, but the reaction stops after a while, and conversion reaches a limiting plateau around 25%, far below the conversion of gelation, which is around 70% for this macrodiol-pluriisocyanate system.³⁴ In the presence of lower amounts of AIBN, the value of the plateau gradually increases and will cross the 70% conversion level at the critical concentration.

The initial slope of the curves displayed Figure 3 are different, indicating that not only the end-

Table III Influence of the Presence of AIBN on Gelation of the Macrodiol-Pluriisocyanate Reaction Catalyzed by Various Organotin Compounds at 25 and 60°C

Catalyst ^a	AIBN (%)	Gelation at 25°C (min)	Gelation at 60°C (min)
SnOc_2	0	50	5
	0.05	No gel	No gel
DBTDL	0	600	70
	1.0	600	90
DBTEH	0	600	70
	1.0	600	90

^a Catalyst concentration, 0.1%.

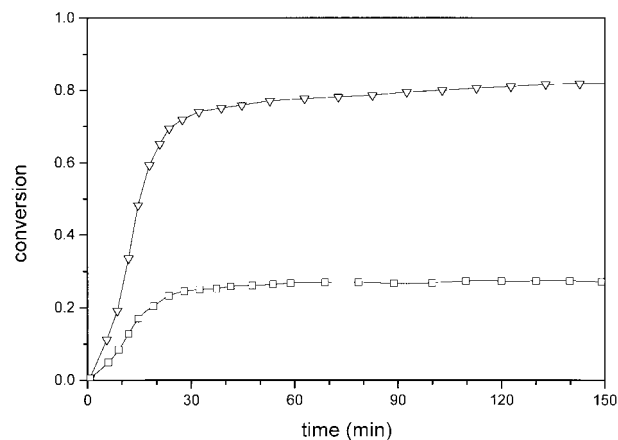


Figure 3 NCO conversion versus reaction time for the catalyzed macrodiol-pluriisocyanate reaction at 60°C. $[\text{SnOc}_2] = 0.1\%$. $[\text{AIBN}] = (\nabla) 0\%$; $(\square) 1.0\%$.

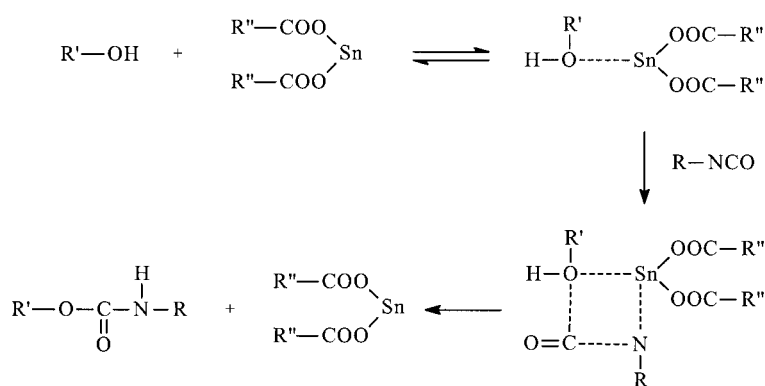
conversion of polyurethane is affected by the presence of AIBN, but also the rate of the polyaddition, thus confirming differences in gel time, as mentioned before.

Catalysis by the SnOc_2 -AIBN Pair: Proposed Mechanism

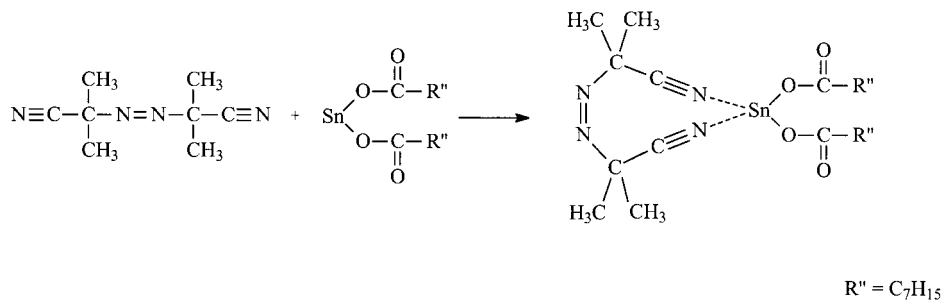
From gel time measurements, conversion monitoring, and equilibrium swelling degrees, interaction between SnOc_2 and AIBN was put in evidence for tin(II)-catalyzed macrodiol-pluriisocyanate reactions. The proposed interpretation involves the basic mechanism^{12,16-19} of catalyzed polyurethane formation. As previously stated, acceleration of the hydroxyl-isocyanate reaction by organotin compounds is a consequence of the formation of a ternary complex between the metal and both the reactants. The tin-alcohol complex-

ation increases the lability of the hydroxyl proton, making it more reactive toward the isocyanate-group nitrogen, itself activated by partial charge transfer to the Sn atom (Scheme 1). In such a complex, the isocyanate and hydroxyl groups are positioned on the same side of the metal in close proximity to each other. Obviously, the steric hindrance around the metal center was found to have strong effects on the rate constants. Also, compounds able to share the catalyst should induce a reaction slowing down. AIBN, aside from generating radicals, can be considered a weak N-donor ligand, therefore, having the possibility to form complexes³⁵ with tin as tertiary amines,³⁶ Schiff-bases,^{37,38} pyridine, and other forms. For evident steric reasons, the metal center would be coordinated to the N atom of the nitrile end-group, preferably to those of the azo group (Scheme 2). As a matter of fact, the competition to complexation between SnOc_2 and AIBN depends on their relative concentrations, and one forms more or less a ternary $[\text{Sn} : \text{NCO} : \text{OH}]$ complex and a binary $[\text{Sn} : \text{CN}]$ complex, respectively, efficient and inactive for the polyaddition.

Moreover, it is well known that AIBN decomposes into two cyanoisopropyl radicals able to initiate numerous free-radical polymerizations. In a nonpolymerizable solvent, in the presence of SnOc_2 , radicals will react with the divalent tin compound, inducing the oxidation tin(II)-tin(IV). The result of this oxidative free-radical reaction would be the formation of a new tetravalent tin carboxylate, as depicted in Scheme 3, with an obviously different catalytic activity than that of SnOc_2 . However, at 25°C, one cannot reasonably refer to the presence of radicals coming from thermal decomposition of AIBN to explain the ob-



Scheme 1



Scheme 2

served reduction of the catalytic activity of SnOc_2 . Moreover, the inhibition effect appears at lower concentrations of AIBN at 25°C than at 60°C , whatever the concentration of SnOc_2 (see Table II). Thus, the formation of a tin–nitrile complex is primary responsible for the rate decrease of the polyaddition when operating at room temperature. Additionally, complexation generates free radicals,¹⁰ not originating from thermal decomposition of AIBN, but from the weakness of the azo linkage, which is under strain because of the cyclic conformation of the complex (Scheme 2). This happens because room temperature decomposition of AIBN by complexation was recently evidenced from the polymerization of methyl methacrylate at temperatures at which AIBN alone would not initiate.⁹

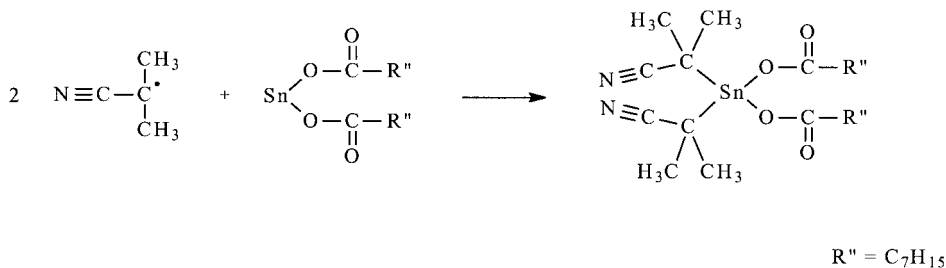
At a temperature of 60°C , the formation of the cyclic complex still occurs, but tin oxidation prevails because the rate constant of AIBN decomposition is higher than at 25°C . Thus, the actual catalyst for the polyaddition is no longer SnOc_2 , but a new tetravalent tin compound. The modification of the electronic environment leads to a decrease of the acceptor effect of the organotin compound, and simultaneously, to an increase of the steric hindrance of the tin atom by two bulky substituents. Thus, oxidation leads to a lower catalytic activity, similar to what is commonly observed in polyurethane technology when replac-

ing SnOc_2 by any organotin(IV) compounds such as DBTDL or DBTEH.

Restoring of the Catalytic Activity of SnOc_2

Whatever their origin, the presence of radicals in the reactive medium unfavorably affects the polyurethane formation. This was also observed³¹ for a similar reaction catalyzed by SnOc_2 , namely, the formation of polydimethylsiloxane networks by end-linking of hydroxyl-terminated prepolymers with tetraalkoxysilane. He et al.³¹ have reported that free radicals inhibited the polycondensation in the presence of oxygen only. Here, however, careful elimination of oxygen from the test tubes by repeated vacuum–nitrogen cycles does not restore the catalytic activity of SnOc_2 .

On the other hand, the addition of a radical scavenger would prevent the oxidative reaction of decomposed AIBN on the tin atom, thus maintaining a high catalytic activity for SnOc_2 . Experiments were made with two relative concentrations of SnOc_2 and AIBN, chosen because the medium does not gel. For one catalytic system, AIBN was the majority, whereas for the second system, SnOc_2 and AIBN were in equimolar amounts, according to the proposed cyclic complex (see Scheme 2). Polyadditions were carried out in the presence of various amounts of TBPC at 25 and 60°C to emphasize the role of radicals at



Scheme 3

Table IV Effect of the Concentration of TBPC on the Catalytic Activity for Two Different SnOc₂-AIBN Pairs

TBPC (%)	Catalytic System ^a : 0.2% SnOc ₂ + 0.5% AIBN		Catalytic System ^b : 0.1% SnOc ₂ + 0.1% AIBN	
	Gelation at 25°C (min)	Gelation at 60°C (min)	Gelation at 25°C (min)	Gelation at 60°C (min)
0	No gel	480	No gel	No gel
0.03	—	—	No gel	16
0.05	No gel	10	No gel	13
0.10	—	—	No gel	17
0.20	No gel	11	—	—
0.30	—	—	No gel	25
0.40	—	—	No gel	120
0.50	No gel	38	No gel	180
1.0	No gel	90	—	—

^a Molar ratio [SnOc₂]/[AIBN] = 0.24.

^b Molar ratio [SnOc₂]/[AIBN] = 1.0.

In the absence of AIBN, gelation occurs after 4–5 and 45–50 min at 25° and 60°C, respectively.

these temperatures. The results are reported in Table IV. At 60°C, the radicals issued from thermal decomposition of AIBN are scavenged by TBPC, and gelation can take place after a short inhibition delay. With increasing concentration of TBPC, the time to gel goes through a minimum, close to the value obtained for gelation without AIBN, then increases again significantly (Fig. 4). Explanation of this could be that some interaction between SnOc₂ and TBPC as white particles, not yet characterized, forms in the solution when concentration of TBPC exceeds 0.3% (which corresponds to a molar ratio [TBPC]/[SnOc₂] of 3).

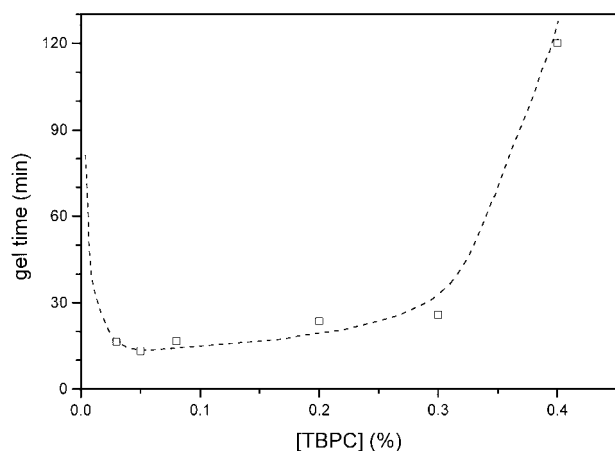


Figure 4 Gelation of the catalyzed macrodiol-pluriisocyanate reaction in the presence of AIBN and various amounts of TBPC at 60°C. [SnOc₂] = 0.1%; [AIBN] = 0.05%.

Thus, at least up to a given concentration, TBPC is an efficient protection of the catalytic activity of SnOc₂.

At 25°C, gelation cannot be restored, within a reasonable time, even in the presence of TBPC. This indicates that complexation between SnOc₂ and AIBN occurs prior to oxidation of SnOc₂ and causes deactivation of the latter.

CONCLUSION

The decrease of catalytic activity of stannous octoate due to the presence of AIBN originates from the competition, which depends on the temperature, of two concurrent mechanisms, namely (1) the formation of a coordination complex between the tin atom of SnOc₂ and the two nitrile nitrogens of AIBN; and (2) the oxidative free-radical reaction of divalent to tetravalent tin. Use of appropriate amounts of a radical scavenger would allow SnOc₂ to recover its efficiency in polyurethane formation. This study about the interaction between SnOc₂ and AIBN is not only academic research but has a practical importance when preparing polyurethane-based interpenetrating polymer networks by a one-shot process. As also shown previously for the polymerization of methyl methacrylate, the presence of the particular SnOc₂-AIBN pair significantly modifies the kinetics of network formation of both components in an IPN compared individually to their kinetics. This is to be taken into account because control of

relative kinetics of formation is of crucial importance for determination of the extent of phase separation, which in turn is responsible, among other parameters, for the properties of IPNs.

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