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The Role of Tin(II) Octoate - Azobisisobutyronitrile Complex in the Formation Rate of the Respective Networks in Simultaneous Interpenetrating Polymer Networks

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SUMMARY: Simultaneous interpenetrating polymer networks (IPNs) based on polyether polyurethane (PUR) and poly(methyl methacrylate-co-trimethylolpropane trimethacrylate) (PMMA) were prepared in bulk at 60°C, using tin(II) octoate and azobisisobutyronitrile (AIBN) as pur polymerization catalyst and free-radical initiator, respectively. The kinetics of the PUR network formation, PMMA network formation as well as PUR/PMMA IPN formation were studied independently by Fourier transform infra-red spectroscopy. The simultaneous formation of the two networks interfered with each other, although they follow different polymerization mechanisms. Mainly two effects concerning the free-radical polymerization have been seen: a decrease of the initiation period and an earlier appearance of the Trommsdorff effect when increasing the concentration of the catalyst. On the other hand, the presence of AIBN in the reaction medium drastically reduced the catalytic efficiency of the organotin compound. An explanation of these results for this particular activating system could be the formation of a cyclic equimolar complex by coordination of the nitrile groups of AIBN with the Sn(II) atom. Complexation both reduces the effective catalyst concentration and induces steric constraints in the azo bond of AIBN, rendering this linkage weaker and more easily cleavable and allowing an early decomposition into radicals of the complexed AIBN. The maximum rate corresponds to a 1:1 complex. Further, decomposition into radicals leads to tin oxidation and formation of a new tetravalent organotin compound, the catalytic activity of which is lower than that of pure tin(II) octoate for the isocyanate-alcohol reaction.

Introduction

Interpenetrating polymer networks (IPNs) are combinations of two or more cross-linked polymers held together by permanent entanglements and obtained under special preparation methods.[1] One process industrially suitable was a one-step (*in situ*) polymerization in which all monomers or prepolymers are first mixed together before polymerization or crosslinking of either component. Such synthesis requires noninterfering routes for the two polymerizations, typically a polyaddition or polycondensation mechanism and a chain

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polymerization. Among the various IPNs prepared to date, combinations of polyurethane (PUR) and poly(methyl methacrylate) (PMMA) have been thoroughly investigated, mainly because these polymer pairs are widely used in numerous applications.[2,3)]

Most IPNs exhibit a limited phase-separated structure, compared to other types of blends. Among the parameters which control the extent that IPNs undergo phase separation, the relative reaction rates of network formation play a predominant role.[4,5)] Studies on kinetics effects involved in IPN formation in relation with their morphology and properties have been the subject of a recent review.[6)] In previous publications on simultaneous polyurethane/ poly(methyl methacrylate) (PUR/PMMA) IPNs, we have reported that a key variable to obtain a wide spectrum of physicochemical properties for a given composition was the relative rates of the formation reactions.[7,8)] Control of the reaction conditions was achieved simply by changing temperature, choice and amount of catalyst or free-radical initiator or both.[9)] For instance, when the concentration of catalyst is decreased, the formation of the PUR network becomes slower, but more than expected, and the kinetics of formation of the PMMA network are also modified. The explanation for the latter effect, not seen in the case of *in situ* sequential synthesis,[10)] should be found either in the presence of still reactive compounds (isocyanate, alcohol, catalyst), in the medium of the precursors of the PUR network, or the rheological change, typically increase of viscosity, of the medium, due to the polyaddition reaction that proceeds simultaneously.

As a part of a continuing study of the kinetics of formation of IPNs, the objective of the present work was to clarify the role of organotin compounds, catalysts for the formation of PUR, on the kinetics of the copolymerization of methyl methacrylate with trimethylolpropane trimethacrylate (TRIM), and, conversely, the influence of the presence of radicals, obtained by the thermal decomposition of azobisisobutyronitrile (AIBN), on the catalyzed PUR polymerization.

Experimental

Materials and Synthesis

The elastomeric PUR network was based on a polyoxypropylene macrodiol (POPG) reacted with a plurifunctional isocyanate, while the PMMA network was obtained by the copolymerization of methyl methacrylate with a small amount (5 wt-%) of TRIM. Simultaneous PUR/PMMA IPNs were prepared in bulk at 60 °C from homogeneous mixtures of all the previous reactants, using an organotin compound and AIBN as PUR polymerization catalyst and free-radical initiator, respectively. Experiments were conducted either in nitrogen-purged Pyrex tubes dipped into a water bath or in an infra-red cell, formed by two NaCl plates, placed in a heating chamber.

The macrodiol, Arcol 1020, kindly donated by Arco Chemicals, had an average molar mass of 2000 $g{\cdot}mol^{-1}$ It was dried at 80 °C for 5 h under vacuum just before use. The branched reactant, Desmodur L75, a trimethylol propane/toluene diisocyanate adduct, was obtained from Bayer AG and used as received. The monomers, MMA from Merck and TRIM from Degussa, contained 100 ppm hydroquinone and were dried over 4 Å molecular sieves but not otherwise purified. AIBN (Merck) was recrystallized from methanol before use. The organotin compounds were used as received. Very sensitive to oxygen, tin(II) octoate ($SnOc_2$) (K29, Goldschmidt) was stored under nitrogen at low temperature. The tin content: was 29.3% by weight. Dibutyltin dilaurate (DBTDL) (K19, Goldschmidt) contained 18.5% tin by weight. Dibutyltin bis(2-ethylhexanoate) (DBTEH) (Alfa Johnson Matthey), 22.9% tin by weight, was used in powdery form.

Characterization

A Nicolet 60SX Fourier transform infra-red (FTIR) spectrometer equipped with a Specac heating chamber was used to follow the reaction kinetics. The spectra were recorded at 2 cm^{-1} resolution and 32 consecutive scans were collected for signal averaging. Reaction conversion was calculated from the change with time of the normalized absorbance of the isocyanate peak at 2275 cm^{-1} and of the C=C stretching vibration at 1639 cm^{-1}, to confirm the validity of the Beer-Lambert law. Sample thickness was 25 μm.

UV spectra of AIBN/$SnOc_2$ binary mixtures in solution in ethyl acetate were recorded on a Shimadzu UV-214 double beam spectrophotometer in the range 320 – 420 nm.

Gel points were determined visually as being the conversion at which the reaction medium would no longer flow, i.e. when a small needle would no longer penetrate the reaction medium. Swelling experiments were made on small rectangular pieces immersed in ethyl acetate. The solvent was renewed every two days. Equilibrium swelling was amply attained after 10 days of immersion at room temperature. The samples were then removed from the solvent and immediately weighed. Afterwards, the swollen samples were carefully dried in a vacuum oven and weighed again. The swelling degree is defined as being the ratio of the weights of swollen to dry sample.

The volume of nitrogen evolved in the course of AIBN decomposition was measured with a thermostatted azotometer containing suitable quantities of organotin compounds dissolved in ethyl acetate. Prior to the measurement, the apparatus was deoxygenated by repeated cycles of vacuum and purified argon. The volume of nitrogen collected in a calibrated gas burette was determined with a precision of ± 0.01 ml.

Results and Discussion

1. Influence of Tin(II) Octoate on Free-Radical Polymerization

The kinetics of copolymerization of MMA with TRIM during the formation of *in situ* simultaneous 50/50 PUR/PMMA IPNs are presented in Fig. 1, using various amounts of tin(II) octoate ($SnOc_2$), the catalyst of the isocyanate/alcohol reaction. Despite constant reaction temperature (60°C), constant amounts of cross-linker (5 wt-%) and of free-radical initiator (AIBN, 1 wt-%), the C=C conversion versus time curves are not superimposable, indicating that the simultaneous formation of the polyurethane network kinetically interfered with the formation of the methacrylic network. Three effects can be seen: (i) the initiation period is reduced with increasing concentration of $SnOc_2$; however, propagation rates are identical since the slopes of the various curves are the same between 20% and 80% conversion; (ii) the Trommsdorff effect appears earlier with increasing concentration of $SnOc_2$; and (iii) contrary to the bulk polymerization of MMA, a final conversion of 100% is reached in every case.

The last effect, previously seen with *in situ* sequential PUR/PMMA IPNs$^{10)}$, can be explained by the dilution of the reaction medium and by a glass transition temperature that is lower than the temperature of synthesis. The explanations of the two other effects may be as follows: viscosity change of the reaction medium, and the influence of the $SnOc_2$ on initiation of the free-radical polymerization. At a given time, it is evident that an increase of catalyst concentration leads to a faster formation of PUR network and, therefore, to an increase of viscosity of the reactive medium. The consequence is a decrease of the initiation period of the free-radical polymerization and an earlier appearance of the Trommsdorff effect. The fact that the system forms branched points should also be taken into account. However, the conversion of MMA at the gel point cannot be calculated, neither theoretically nor experimentally, since gelation depends on the synthesis conditions.[11,12]

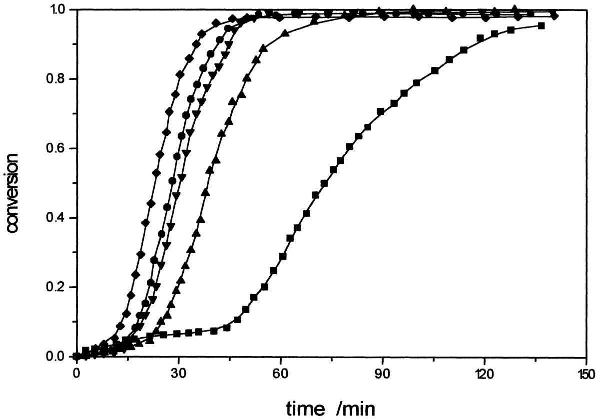

Fig. 1: C=C conversion versus reaction time for the copolymerization of MMA with TRIM during syntheses of *in situ* simultaneous 50/50 PUR/PMMA IPNs at 60°C. Formation of the PUR networks was catalyzed by various amounts of $SnOc_2$: (■) 0.1 wt-%; (▲) 0.2 wt-%; (▼) 0.35 wt-%; (●) 0.5 wt-%; (◆) 1.0 wt-%.

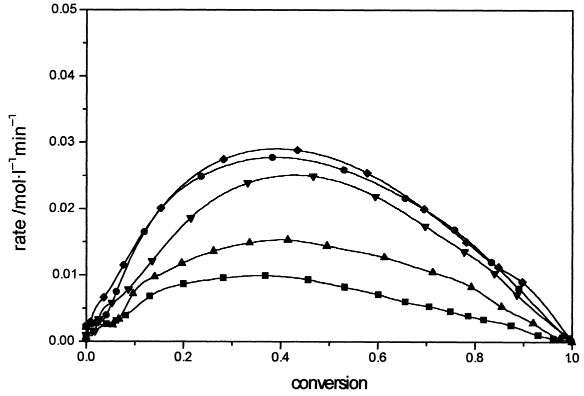

Fig. 2: MMA/TRIM copolymerization rates during syntheses of *in situ* simultaneous 50/50 PUR/PMMA IPNs at 60°C. Amount of $SnOc_2$ in the reaction medium: (■) 0.1 wt-%; (▲) 0.2 wt-%; (▼) 0.35 wt-%; (●) 0.5 wt-%; (◆) 1.0 wt-%.

According to Rosenberg and Flodin,13) gelation occurs when the slope of the kinetics curves changes suddenly; this corresponds in our case to a conversion range of 5% to 11%, which is also the beginning of the Trommsdorff effect.

The variation of the copolymerization rate of the methacrylic components versus conversion of C=C double bonds is shown in Fig. 2. It can be seen that the rate increases significantly from about 10% conversion; however, the regular change of the rate profile with the concentration of $SnOc_2$ is difficult to explain. Replacement of the simultaneously developing polyurethane system by an inert solvent would be useful to suppress the influence of viscosity and to determine better the role of $SnOc_2$. Therefore, only the formation of PMMA networks in bulk or in solution is considered hereafter.

Table 1 gives the results of the copolymerization of MMA and TRIM in the presence of AIBN and $SnOc_2$ at two temperatures, 25 °C and 60 °C, respectively. Experiments were conducted in the dark to prevent chance photopolymerization. As expected, in the absence of AIBN or $SnOc_2$, no polymerization occurs. 25 °C Also, at room temperature, neither AIBN nor $SnOc_2$ alone initiates the chain copolymerization. At 25 °C, only the couple AIBN/$SnOc_2$ leads to a network, in about 3 h or 24 h, in bulk or in solution, respectively. At 60 °C, $SnOc_2$ is still inactive towards the methacrylic monomers, but, combined with AIBN, gelation occurs twice faster than with only AIBN, thus confirming the synergistic effect of the couple AIBN/$SnOc_2$ on the kinetics of free-radical copolymerization of MMA and TRIM in simultaneous IPNs.

Table 1: Gelation of the methacrylic monomers under various conditions.

[AIBN] (wt-%)	[$SnOc_2$] (wt-%)	MMA-co-TRIM			
		in bulk a)		in 34% ethyl acetate b)	
		60°C	25°C	60°C	25°C
0	0	no gel	no gel	no gel	no gel
0	1	no gel	no gel	no gel	no gel
1	0	gel in 20 min	no gel	gel in 32 min	no gel
1	1	gel in 8 min	gel in 180 min	gel in 15 min	gel in 24 h

a) Yield after 15 h of reaction. b) Yield after 60 h of reaction.

Under the same experimental conditions, replacement of $SnOc_2$ by organotin(IV) compounds, like dibutyltin dilaurate (DBTDL) or dibutyltin bis(2-ethylhexanoate) (DBTEH), does not leads to the formation of a methacrylic network when associated with AIBN at room temperature. At 60°C, gelation occurs, but significantly more slowly than when using pure AIBN. Hence, contrary to the couple AIBN/$SnOc_2$, combinations of AIBN with tetravalent organotin compounds have no synergistic effects on the free-radical polymerization of MMA, thus confirming the particular role played by $SnOc_2$ due to its bivalent tin.

2. Influence of the Presence of Radicals on Tin-Catalyzed Polyurethane Formation

Polyurethane networks were prepared at 60°C and 25°C by replacing the methacrylic monomers by an inert solvent like ethyl acetate. The isocyanate–alcohol reaction was catalyzed by $SnOc_2$ in the presence of various amounts of AIBN. At 60°C, using 1.0 wt.-% $SnOc_2$, the reaction is not very sensitive to the presence of AIBN. However, at 25°C, the gel time of the medium increases gradually with increasing amounts of AIBN (Fig. 3). When decreasing the amount of $SnOc_2$ from 1.0 to 0.1 wt-%, gelation becomes more and more difficult, as expected, but with an additional dependence on concentration of AIBN and temperature. For example, with 0.3 wt.-% $SnOc_2$, gelation occurs in 23 min in the absence of AIBN, while it takes more than 7 h in the presence of 0.5 wt-% AIBN (at room temperature).

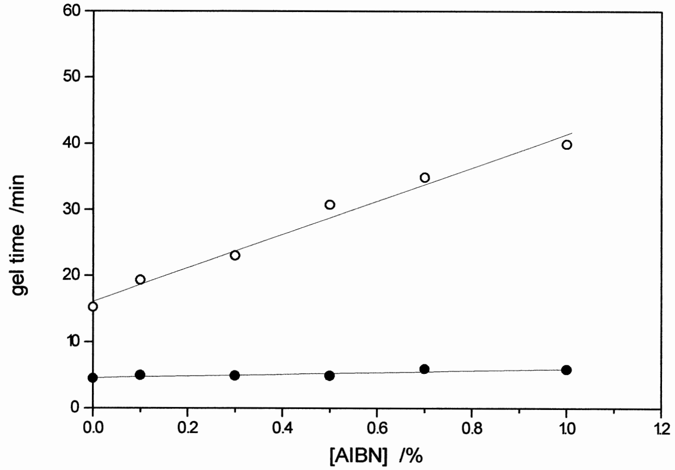

Fig. 3: Influence of the concentration of AIBN on the gel time of polyurethane, using 1.0 wt-% tin(II) octoate as catalyst. Reaction temperature: (●): 60°C, (o): 25°C.

At 0.1 and 0.2 wt-% $SnOc_2$, very small quantities of AIBN are sufficient to inhibit gelation (Fig. 4).

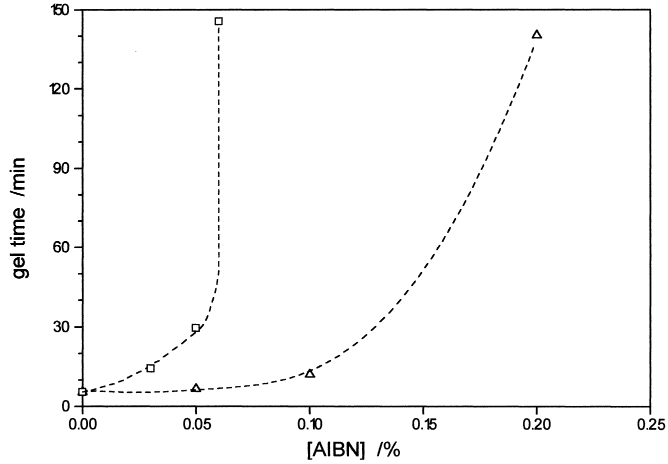

Fig. 4: Gel times of polyurethane at 60 °C in the presence of various amounts of AIBN. Catalyst: $SnOc_2$: (□) 0.1 wt-%, (△) 0.2 wt-%.

These experiments have been repeated using other organotin catalysts, namely, DBTDL and DBTEH. Contrary to $SnOc_2$, which is a bivalent organotin compound, DBDTL and DBTEH are tin(IV) compounds. No inhibition of gelation due to the presence of AIBN was observed for the two temperatures studied, see Table 2.

Table 2: Influence of the presence of AIBN on gelation of tin-catalyzed PUR.

organotin compound[a]	[AIBN] (wt-%)	gel time at 60°C	gel time at 25°C
$SnOc_2$	0	5 min	50 min
	0.1	no gel	no gel
DBTDL	0	75 min	>12 h
	1.0	90 min	10 h
DBTEH	0	75 min	>12 h
	1.0	90 min	10 h

[a] concentration: 0.1 wt.-% (approx. 2×10^{-3} mol·l^{-1})

The PUR networks thus prepared were characterized by their equilibrium swelling degrees in ethyl acetate. A value of 5.4 ± 0.4 was found for all samples, independent of the nature and amount of the catalyst, and of the presence or the absence of AIBN, except for those samples that took a long time to gel. One comes to the conclusion that interactions occur between AIBN and tin (II) compounds, and not between AIBN and tin(IV) compounds.

Inhibition of the tin(II)-catalyzed polyurethane formation by AIBN is seen in Fig. 5 where the conversion of isocyanate is plotted versus time. In the presence of AIBN, the network forms with a slightly lower initial rate than in the absence of AIBN, but afterwards, the reaction stops at a conversion that is lower than that of gelation (ca. 70% for this system). When decreasing the amount of AIBN in the AIBN/SnOc$_2$ binary system, the level of the plateau progressively increases up to gelation.

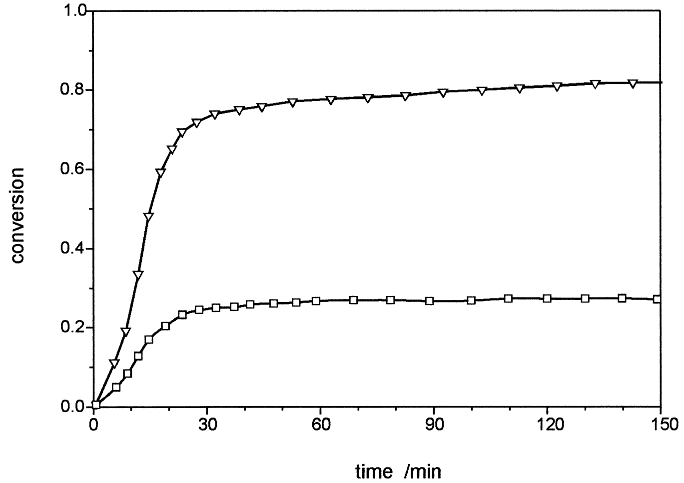

Fig. 5: Conversion – time curves for polyurethane formation at 60°C as revealed by FTIR spectroscopy. [SnOc$_2$] = 0.1 wt-%, [AIBN] = 0 wt-% (▽), 1.0 wt-% (□).

The "poisoning" of the catalytic activity of SnOc$_2$ by AIBN can be explained by the characteristic properties of tin(II) compounds with respect to the mechanism of the isocyanate–alcohol reaction. The actual reaction mechanism is still uncertain in spite of numerous investigations, but it is assumed that the reaction proceeds with formation of intermediate complexes.[14-16)] The complex formation could occur in two steps, first with activation of the hydroxyl group and formation of a ternary complex with the isocyanate group by coordination with the oxygen and nitrogen atoms, thus increasing the electrophilic nature of the isocyanate group.[17)] Urethane formation could then take place by proton rearrangement. Activation of isocyanate–alcohol reactions comes from the donor–acceptor complex-forming ability of tin having free 5d orbitals in low energy levels.[18)] The rate of urethane formation is further dependent on the rate of dissociation of the labile complexes. Thus, the efficiency of catalysts can be very dependent upon the stability of these complexes, which, in turn, are determined by the nature of the substituents, and the configuration and electronic structure of the coordination complex.

The thermal decomposition of AIBN generates two isobutyronitrile free-radicals which can react with $SnOc_2$ to form a new tetravalent organotin compound which can also be a catalyst for the urethane reaction, but with much lower efficiency.[19)] Oxidation is described by the following reaction:

$$2CN(CH_3)_2C\bullet + :Sn(OCOC_7H_{15})_2 \longrightarrow (CN(CH_3)_2C)_2Sn(OCOC_7H_{15})_2$$

If the oxidation of $SnOc_2$ by radicals is the real reason of decrease of the catalytic activity, then the addition of a free-radical scavenger like 4-tert-butylpyrocatechol (TBPC) should restore it. Table 3 shows the influence of various amounts of TBPC on PUR gelation. The reference gel time (in the absence of AIBN) was less than 10 min at 60 °C. Thus, oxidation of tin(II) to tin(IV) by free-radicals is possible at 60°C, but unlikely at 25°C, unless AIBN decomposes into radicals at lower temperatures. Another possibility for decrease in catalytic activity could be a lower amount of the actual catalyst due to some competition between an efficient complexation of $SnOc_2$ with the isocyanate and hydroxyl groups, which can be denoted {NCO:$SnOc_2$:OH}, and an inert complexation of $SnOc_2$ with AIBN, denoted {AIBN:$SnOc_2$}.[20,21)]

Table 3: Effect of the concentration of TBPC on the catalytic activity of $SnOc_2$ in the presence of an equimolar amount of AIBN. [$SnOc_2$] = 0.1 wt-%, [AIBN] = 0.06 wt-%.

[TBPC] (wt-%)	gel time at 60°C	gel time at 25°C
0	no gel	no gel
0.025	16 min	no gel
0.05	18 min	no gel
0.1	17 min	no gel
0.2	25 min	no gel

3. Thermal Decomposition of AIBN and Complexation with Tin(II) Octoate

Studies concerning interactions with the eventual formation of complexes between the nitrile groups of AIBN and organometallic compounds are reported in the literature , but no detailed studies related to the couple AIBN/SnOc$_2$ were found.

UV-spectroscopy allows the direct determination of the concentration of N=N linkages in a solution of azo compounds in ethyl acetate. The optical density, D_t, was measured as a function of time at a wavelength of 345 nm, corresponding to the maximum of absorption of AIBN. A comparative study was undertaken for AIBN solutions, and AIBN/SnOc$_2$ solutions of equimolar composition. The effect of the addition of SnOc$_2$ on the rate of decomposition of AIBN is presented in Fig. 6, according to the following equation:

$$\log\left(\frac{D_0 - D_\infty}{D_t - D_\infty}\right) = k_d \times t$$

where D_0 is the initial optical density, and D_∞, the residual optical density. For AIBN, $D_\infty = 0$ and for the AIBN/SnOc$_2$ binary system, $D_\infty = 0.053$.[22)]

As shown in Fig. 6, the decomposition of AIBN obeys first-order reaction kinetics in the absence or presence of SnOc$_2$. From the slopes of the lines, values of the rate constant of decomposition of AIBN, k_d, were determined. At 60°C, the values of k_d were 4.5×10^{-6} sec^{-1} and 7.7×10^{-6} sec^{-1} in the absence and presence of SnOc$_2$, respectively. The value for pure AIBN was low, compared to the values taken from literature.[22)] This may be explained by our experimental conditions: AIBN was used as received, without recrystallization (contrary to most authors), and the solutions were not freed from air. Hence, as reported by Van Hook[23)], some peroxides absorbing at the same wavelength as AIBN may form, thus lowering the decomposition rate constant.

In the presence of SnOc$_2$ the decomposition rate constant of AIBN at 60°C is increased by a factor of 1.7, and the hypothesis of a complex between AIBN and SnOc$_2$ would explain a higher decomposition rate constant for the AIBN/SnOc$_2$ system. In fact, several authors have reported,[21,24)] and even isolated,[25)] similar complexes between AIBN and organometallic compounds. On the basis of a shift of the nitrile peak (2245 cm^{-1}) in the infra-red spectrum of the binary system, Hirano *et al*[26)] assumed the formation of a complex. In contrast, no significant shift (3 cm^{-1}) was observed for the AIBN/SnOc$_2$ system, but this does not exclude any complexation since, from periodic table considerations and steric effects, interactions would be weaker with SnOc$_2$ than with AlEt$_3$. Another shift, occurring in the opposite direction

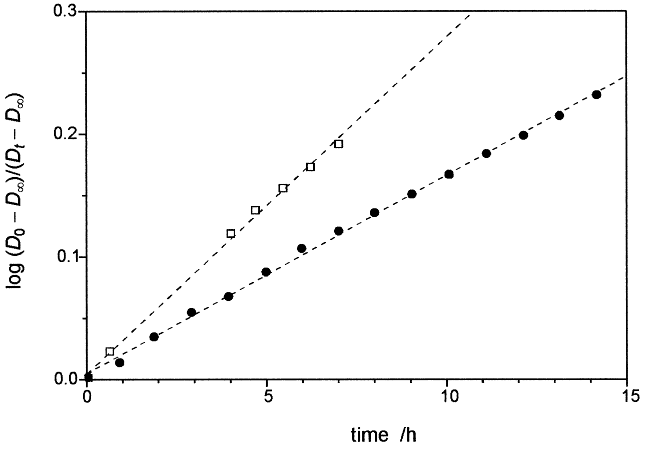

Fig. 6: Thermal decomposition of AIBN at 60°C in ethyl acetate in the absence (●) or in the presence (□) of SnOc$_2$ from UV measurements. [AIBN] = 8.9×10^{-2} mol·l^{-1}. [SnOc$_2$]/[AIBN]=1.

to the shift of the nitrile peak, and therefore to be considered, was observed in the 1175–1185 cm^{-1} region. It was assigned to skeletal vibrations, and suggests conformational changes with the appearance of some constraints in the N≡C–C–N=N– linkages. However, the most significant spectral change was observed in the 1550–1620 cm^{-1} region with the splitting of the strong broad band for pure tin(II) octoate into two narrow peaks for the AIBN/SnOc$_2$ system. These peaks, which are always obtained for tetrasubstituted tin compounds of the general formula R_nSnX_{4-n}, e.g., dibutyltin dilaurate, may be attributed to COO antisymmetric stretching; the change can be used as a good indicator of the valency state of tin and is clear evidence for complexation. Unfortunately, a change in the stretching frequency of the Sn–O bond at about 300 cm^{-1} could not be reached because it was outside the range of the spectrometer.

The volumetric determination of nitrogen generation during the decomposition of AIBN alone, and of the AIBN/SnOc2 binary system was undertaken to complete the previous UV analysis, and to emphasize a possible AIBN/SnOc2 optimum ratio that would give the highest decomposition rate. Assuming that the thermal decomposition of AIBN is a first-order process, the rate can be expressed by the kinetics expression:

$$\log(V_t - V_\infty) = -k_d \times t$$

where V_t is the volume of nitrogen evolved up to time t, and V_∞ is the volume of N_2 evolved during complete decomposition.

Plots of $\log(V_t - V_\infty)$ versus time for various [SnOc2]/[AIBN] ratios are displayed in Fig. 7. They clearly show the influence of the amount of SnOc2 on the decomposition of AIBN. The slope of the straight lines gives the values of the decomposition rate constant k_d (Table 4). With increasing amount of SnOc2, the decomposition rate of AIBN progressively increases, and reaches a plateau before decreasing for [SnOc2]/[AIBN] > 1. The maximum value of k_d corresponds to an increase of 1.7 times the value of k_d found for the decomposition of AIBN alone, thus confirming results obtained by UV spectroscopy.

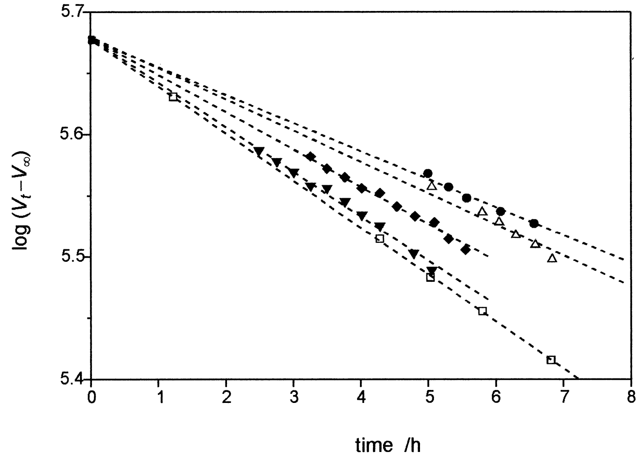

Fig. 7: Effect of tin(II) octoate on the thermal decomposition of AIBN at 60°C in ethyl acetate. [SnOc2]/[AIBN] = 0 (●), 0.5 (△), 0.75 (▼), 1.0 (□), 2.0 (◆). [AIBN] = 8.1×10^{-2} mol·l^{-1}.

Cyclic complexation of the two nitrile groups by the tin atom would induce strain into the N=N and C–N linkages by its steric restriction, rendering these bonds weaker and easily cleavable, and consequently would increase the rate of decomposition at a given temperature. The formation of such an {AIBN:$SnOc_2$} complex makes possible the polymerization of methyl methacrylate at temperatures (<50°C) at which AIBN alone would not initiate[27)]. The lower value of k_d for $[SnOc_2]/[AIBN] = 2$ is explained by the presence of tin(II) octoate in excess in the medium giving a lower probability of encounter between one molecule of $SnOc_2$ and one molecule of AIBN to form an equimolar complex. Another possibility is the complexation of each of the nitrile groups, each with a different atom of tin, making the formation of the cyclic complex impossible. The results are consistent with the formation of a 1:1 complex with the following structure:

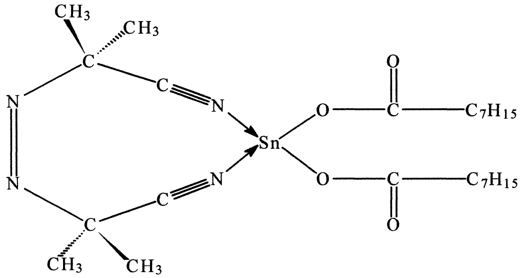

Table 4: Dependence of the AIBN decomposition rate constant on the concentration of tin(II) octoate at 60°C.

$[SnOc_2]/[AIBN]$ [a)]	$10^6 \times k_d$ /s^{-1}
0	6.4
0.5	7.1
0.75	9.8
1.0	10.8
1.5	10.8
2.0	8.6

[a)] molar ratio

Conclusion

Interference between AIBN and tin(II) octoate, the free-radical initiator and the organotin(II) catalyst, respectively used for the synthesis of simultaneous interpenetrating polymer networks based on PUR and PMMA was revealed from kinetics measurements. Mainly two effects have been seen: (i) a decrease of the initiation period with no change in the propagation and termination rates of PMMA when increasing the concentration of $SnOc_2$, and (ii) a decrease in the catalytic efficiency of $SnOc_2$ due to the presence of AIBN. Replacing $SnOc_2$ by an organotin(IV) compound or adding a free-radical scavanger would suppress the cross-influence of the reactants. An explanation of these results would be the formation of a cyclic equimolar complex by the coordination of the nitrile groups of AIBN with the bivalent tin atom. Complexation both reduces the effective catalyst concentration, and induces steric constraints in the azo bond of AIBN. This allows the early decomposition into radicals of the complexed AIBN, and therefore constitutes a new possibility to accelerate radical polymerizations. The proposed explanation might even be valid more generally for other organometallic acceptors that could in principle coordinate with nitriles. However, this possibility remains to be investigated.

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