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COMMUNICATION

Silicone curing and polyurethane preparation promoted by latent organotin catalysts

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The use of new latent organotin catalysts has been investigated for silicone curing and polyurethane preparation. These functional tetraorganotins are inactive at room temperature and liberate *in situ* the active species, diorganotin dicarboxylates, when heated. They confer long pot-lives to the mixtures in which they are incorporated. Upon heating, these mixtures are rapidly cured or polymerized after a short activation period.

Keywords: Silicone, polyurethane, curing, tetraorganotin, latent, organotin catalyst, decomposition, diorganotin dicarboxylates

INTRODUCTION

Diorganotin compounds are mainly used as PVC stabilizers in the chemical industry. They also have important applications as catalysts in other areas, such as silicone curing,[1–3] polyurethane preparation[4,5] and esterification reactions,[6] because of their high efficiency, low cost and moderate toxicity.[7–9] For silicones, the curing of linear polymer chains necessary to develop the required elastomeric properties can be obtained by either an addition or a condensation reaction. The first case involves the platinum-catalysed addition of silicon–hydrogen bonds of linear hydrogenopolyorganosiloxanes to vinyl groups carried by other polyorganosiloxane chains. In the second case the creation of the silicon–oxygen–silicon network is obtained by condensation of terminal silicon-hydroxyl groups with a curing agent, either a tetra-alkoxysilane (SiOH/SiOR condensation) or a hydrogenopolysiloxane (SiOH/SiH condensation). Both processes are catalysed by diorganotin dicarboxylates. In the polyurethane industry, high production rates are essential and the use of catalysts is necessary. Diorganotin dicarboxylates are very often used in this context, often associated with tertiary amines for better efficiency due to a synergistic effect.[10] However, for either silicones or polyurethanes, such high efficiency may cause inconvenience as the condensation reactions start as soon as reactants and catalysts are mixed together. A rapid decrease in fluidity of the mixture results, which may pose a problem for the user. In order to avoid this drawback, an ideal catalyst might be inactive at room temperature to induce infinite shelf- or pot-lives and regain full activity at oven temperature.[11] To our knowledge, only one system of latent catalysts based on a tin reagent has been reported at this time. It has been applied to polyurethanes and involves the adduct of a tin carboxylate on a sulphonylisocyanate which can be decomposed *in situ* by the addition of water or alcohol to give a species active for catalysis.[12]

RESULTS

We have started investigations intended to design new organotin catalysts inactive at room temperature, but which could be activated at will, i.e. easily transformed into diorganotin dicarboxylates, the active species for silicone curing or polyurethane preparation. As precursors of diorganotin dicarboxylates, we have chosen tetraorganotins with two acyloxy groups in the β-position, because tetraorganotins usually lack catalytic activity. These thermally sensitive compounds are easily decomposed into diorganotin dicarboxylates

$$Bu_2Sn(CH_2CHR^1OCOR^2)_2 \xrightarrow{\Delta} Bu_2Sn(OCOR^2)_2 + 2\,CH_2{=}CHR^1 \quad [1]$$

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Table 1 SiOH/SiOR condensations

Run	Organotin compound	Pot-life[a] (min)	Gel time[b] (min)	T (°C)
1	$Bu_2Sn(OCOCH_3)_2$	10^2	5	120
2	$Bu_2Sn(CH_2CH_2OCOCH_3)_2$	7×10^3	30	120
3	$Bu_2Sn(OCOCH(C_2H_5)n\text{-}C_4H_9)_2$	5×10^2	5	140
4	$Bu_2Sn(CH_2CH_2OCOCH(C_2H_5)n\text{-}C_4H_9)_2$	14×10^3	30	140
5	$Oct_2Sn(OCOCH(C_2H_5)n\text{-}C_4H_9)_2$	10^3	5	140
6	$Oct_2Sn(CH_2CH_2OCOCH(C_2H_5)n\text{-}C_4H_9)_2$	$>2 \times 10^4$	30	140

[a]Time necessary to reach the gel state at room temperature. [b]Time necessary to reach the gel state at temperature T.

Such an intramolecular process is especially favourable for use in complex industrial reaction mixtures, avoiding a less likely bimolecular reaction. The decomposition mechanism was found to be monomolecular or pseudomonomolecular and a study of substituent effects on the decomposition rates suggested a desynchronized six-membered transition state in which the carbon–oxygen bond is broken prior to the tin–oxyen bond being established.[13, 14]

Two conditions must be satisfied to show that bis(2-acyloxyalkyl)diorganotins can really be used as latent catalysts:

(1) The compositions containing silicone oil, curing agent and latent catalyst, or diol, isocyanate and latent catalyst, must be more stable at room temperature than compositions where the latent catalyst is replaced by the corresponding diorganotin dicarboxylate.
(2) upon heating, the latent catalyst present in the mixture must quickly liberate the corresponding diorganotin dicarboxylate, and the composition must cure or polymerize rapidly.

The tests for SiOH/SiOR polycondensation were conducted on mixtures composed of α,ω-dihydroxylated polyorganosiloxane oil, tetrapropoxysilane and latent catalyst or diorganotin dicarboxylate. First we compared the behaviour of the mixtures containing (1) the diorganotin dicarboxylates or (2) the latent catalysts at room temperature to observe the differences in pot-life (taken in these experiments as the time necessary for the mixture to gel). The results are given in Table 1. With the latent catalysts (runs 2, 4, 6), pot-lives were found to be at least 20 to 70 times longer than with the corresponding diorganotin dicarboxylates (runs 1, 3, 5). These data demonstrate the much higher stability of the compositions containing a latent catalyst. Secondly, the mixtures were heated and the gel times (given in Table 1), were measured to compare the activity of the diorganotin dicarboxylates with that of the latent catalysts. It is clear that, when heated, the mixtures containing a latent catalyst gelled rapidly, indicating their efficiency: gel times with the latent catalysts are only six times longer than with the corresponding dicarboxylates.

Mixtures composed of α,ω-dihydroxylated polyorganosiloxane oil, a small amount of a hydrogenated polyorganosiloxane oil and the diorganotin dicarboxylate or latent catalyst were set at room temperature and the pot-lives measured. For these SiOH/SiH condensations, pot-lives were taken as the time necessary for the viscosity of the mixture to reach 1500 P. They increased strongly with the latent catalysts by a factor of between 200 and 4000, as shown in Table 2. Indeed, when heated, the catalytic activity was recovered very fast and the gel state was usually reached in only twice the time necessary to gel a mixture containing the corresponding diorganotin dicarboxylate.

The efficiency of the latent catalysts for polyurethane preparation has been tested on mixtures containing 5-isocyanato-1-isocyanatomethyl-1,3,3-trimethylcyclohexane (isophorone diisocyanate), 1,4-butanediol, poly(ethylene glycol) and diorganotin dicarboxylate or latent catalyst. As for the silicone experiments, gel times were measured at room temperature to determine pot-lives and at 100 or 140 °C to ascertain the activity of the new organotin compounds. They are given in Table 3. At room temperature, gel times with the latent catalysts were found to be equal to those of the mixtures containing no tin compound, which means that the latent catalysts were

Table 2 SiOH/.SiH condensations

Run	Organotin compound	Pot-life[a] (min)	Gel time[b] (min)	T (°C)
1	$Bu_2Sn(OCOCH_3)_2$	5	5	110
2	$Bu_2Sn(CH_2CH_2OCOCH_3)_2$	19×10^3	40	110
3	$Bu_2Sn(CH_2CH(CH_3)OCOCH_3)_2$	10^3	10	110[c]
4	$Bu_2Sn(OCOn\text{-}C_{11}H_{23})_2$	10	10	110
5	$Bu_2Sn(CH_2CH_2OCOn\text{-}C_{11}H_{23})_2$	8×10^3	20	110
6	$Bu_2Sn(OCOCH(C_2H_5)n\text{-}C_4H_9)_2$	15	5	140
7	$Bu_2Sn(CH_2CH_2OCOCH(C_2H_5)n\text{-}C_4H_9)_2$	14×10^3	10	140

[a] Time necessary to reach a viscosity of about 1500 P (150 Pa s) at room temperature. [b] Time necessary to reach the gel state at temperature T. [c] At 80 °C the gel time was about 20 min.

completely inactive towards the condensation diol-isocyanate. Gel times measured at 100 or 140 °C revealed that, when heated, the latent catalyst rapidly decomposed to give the active species, which catalysed the polymerization reaction. Times were only about twice as long as with the corresponding tin carboxylates.

CONCLUSION

Bis(2-acyloxyalkyl)diorganotins have been shown to be excellent latent catalysts for silicone curing, either for SiOH/SiOR or SiOH/SiH polycondensation, and for polyurethane preparation. They induce very long pot-lives to the mixture in which they are incorporated and, upon heating, liberate *in situ* the active species which catalyse the curing or the polymerization of the compositions.

EXPERIMENTAL

Each test was repeated at least twice. Average values are given in the Tables.

SiOR/SiOH condensations

In a beaker were placed 60 g of α,ω-dihydroxylated silicone oil (average molecular weight 42 500; 4.7 meq OH/100 g of oil), 0.84 g (3.2 mmol) of tetrapropoxysilane and the organotin catalyst (1.14 mmol). The mixture was well stirred with a spatula for 1 min. Approximately one-half of this mixture was then left at room temperature until the mixture gelled. The other half was placed in an oven at the temperature indicated in Table 1 until the gel state was reached.

SiOH/SiH condensations

In a beaker were placed 23 g of α,ω-dihydroxylated silicone oil (average molecular weight 42 500; 4.7 meq OH/100 g of oil) 1 g of

Table 3 Polyurethane preparations

Run	Organotin compound	Pot-life[a] (min)	Gel time[b] at 110 °C (min)	Gel time[b] at 140 °C (min)
1	None	480		
2	$Bu_2Sn(OCOCH_3)_2$	55	4	3
3	$Bu_2Sn(CH_2CH_2OCOCH_3)_2$	480	8	5
4	$Bu_2Sn(OCOn\text{-}C_{11}H_{23})_2$	100	5	3
5	$Bu_2Sn(CH_2CH_2OCOn\text{-}C_{11}H_{23})_2$	480	8	5
6	$Bu_2Sn(OCOCH(C_2H_5)n\text{-}C_4H_9)_2$	110	5	3
7	$Bu_2Sn(CH_2CH_2OCOCH(C_2H_5)n\text{-}C_4H_9)_2$	480	8	5

[a] Time necessary to reach the gel state at room temperature. [b] Time necessary to reach the gel state at the given temperature.

polyhydrogenomethylsiloxane (SiH content 1.5%) and the organotin catalyst (0.712 mmol). The mixture was stirred with a spatula for 1 min. Approximately half of this mixture was then left at room temperature and its viscosity measured periodically until it reached 1500 P (150 Pa s). The other half was placed in an oven at the temperature given in Table 2 until the mixture gelled.

Polyurethane preparation

In a Schlenk tube under dry nitrogen were added 5.26 g of poly(ethylene glycol) (average molecular weight 1000), 0.80 g of 1,4-butanediol (9 mmol), and 1 cm^3 of a 0.0075 mol dm^{-3} solution of the tin catalyst in dry ether. The solvent was evaporated and 3.94 g of 5-isocyanato-1-isocyanatomethyl-1,3,3-trimethylcyclohexane (isophorone di-isocyanate) (18 mmol) was added. Approximately half of the mixture was then left at room temperature until it gelled to obtain the pot-life and the other half was introduced in an oven at the temperature given in Table 3 until the mixture gelled.

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