Effect of Length of Ligand in Organotin Compounds on Their Catalytic Activity for the Polycondensation of Silicone

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ABSTRACT: Two sets of organotin compounds, that is, one having dibutyl and the other dioctyl groups each with a varying length of a carboxyl group attached to a tin atom, were studied as catalysts for the polycondensation of room temperature vulcanization of hydroxyfunctional polydimethylsiloxane (HOPDMS). The experiments were carried out with the help of a simple and inexpensive piece of equipment called the vibrating needle curemeter (VNC). It has been found that an increase in the length of the carboxyl, as well as the alkyl group bonded to the tin atom, decreases the activity of organotin compounds as catalysts for the polycondensation of HOPDMS. A threshold limit for the difference in catalytic activity of organotin compounds for curing HOPDMS has, for the first time, been established. It has been worked out that when the total number of carbon atoms in the ester and alkyl groups in organotin compounds exceeds 30, then the difference in their catalytic activity reaches a nonmeasurable level by VNC. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2235–2239, 1998

Key words: vulcanization; crosslinking; polycondensation; hydroxyfunctional polydimethylsiloxane

INTRODUCTION

The room temperature vulcanization of hydroxyterminated polydimethylsiloxane (HOPDMS) with alkoxysilane occurs in the presence of certain catalysts, such as amine and carboxylic acid salt of Pb, Zn, Zr, Sb, Fe, Cd, Sn, Ba, Ca, and Mn. Among these, organotin compounds have proved particularly satisfactory because these catalysts do not affect the rate of less-desirable side reactions to a great extent.¹ The system cures by the catalytic condensation of hydroxyl groups of polysiloxane with an alkoxy silane according to a chemical reaction such as shown in structure 1.

Despite the wide variety of these tin compounds used as catalysts for condensation of HOPDMS for over 35 years, the mechanism of the reaction and fate of the catalyst is not well understood.^{1,2} The complexity of the mechanism of this reaction and the uncertainty of the fate of the catalyst is reflected in the fact that the literature values of the order of reaction with respect to tin compounds in the polycondensation of silicone varies from 0.24 to 1.0.2-5 These organotin compounds vary in their activities for curing as catalysts. There are no complete data available on the relative activities of these catalysts on the room temperature vulcanization of HOPDMS in the literature, which is one of the reasons for the lack of understanding of its curing phenomenon. The relatively small number of hydroxyl groups present on the silicone chain and the reason that change of phase take place during crosslinking exclude chemical or spectroscopic methods for monitoring the curing reaction.

In the present work, the catalytic activity of two sets of compounds differing with respect to their carboxylic as well as alkyl groups was assessed on the rate of curing of HOPDMS for over

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30 min by means of a simple and inexpensive instrument called the RAPRA vibrating needle curemeter (VNC). The details of this instrument has been described in an earlier article.³ This instrument records changes in the viscoelastic properties of the sample during the polycondensation of the material.

EXPERIMENTAL

The hydroxy-terminated liquid polydimethylsiloxane used was C18 supplied by Bayer Ltd. (Berkshire, UK). The molecular weight determined by viscometry was 67,000. The crosslinker, vinyltrismethoxyethoxy silane, coded A172, used was supplied by Union Carbide Ltd. (Hertfordshire, UK). Two sets of organotin compounds, that is, one with dibutyl and the other with a dioctyl group, each with varying length of carboxyl groups used as catalysts, were kindly supplied by International Tin Research Institute (ITRI, Middlesex, UK). Carbon tetrachloride was supplied by Merck-Schuchardt (Dorset, UK). These chemicals were used without further purification.

METHOD: EVALUATION OF THE RELATIVE CATALYTIC ACTIVITIES OF CATALYST

Each catalyst solution (in the range of 10% w/w) was made by dissolving weighed amounts of the

catalyst in carbon tetrachloride using a 4-digital balance. To 300 g of HOPDMS, 3.0038 g (1% w/w) of crosslinker was added and spatulated to a homogeneous mixture. Then a calculated, weighed amount of catalyst solution that contained equal amounts, that is, $(5 \pm 0.3) \ 10^{-2}$ g, of organotin compound were mixed with 15-g mixture of HOPDMS and crosslinker. The mixed material was spatulated into polyethylene caps of 2.8-cm inside diameter and 1.5-cm depth; it was deployed to the VNC's needle, set for vibration at 40 Hz. The depth of the needle in the material was kept constant, that is, 0.3 mm each time. The suitability of these constants has been determined by the author.⁶ The curve for the activity of each catalyst was recorded over 30 min. The calculated deflection in millivolts at 30 min for each catalyst was plotted against the number of carbon in the ester groups of the organotin catalysts.

RESULTS AND DISCUSSION

The catalytic activity of both of the organotin carboxylates, that is, butyl and octyl, for the curing of HOPDMS are presented in graphical form. In each case, the number of carbons in the carboxyl groups of the organotin catalyst is plotted against the deflection in millivolts for the curing of HOPDMS at 30-min time.

Graph (a) of Fig. 1 shows the variation of deflection with the number of carbons in the carboxyl group of the butyl series of compounds, while Graph (b) depicts the activity of the octyl series of organotin compounds. It is clear from Graph (a) that there is a decrease for increase in chain length of carboxyl ligand of the butyl series of catalyst. This decrease follows up to the point when the carboxyl moiety reaches a 12-membered carbon.

In the case of the octyl series [Graph (b)], there is also a decrease in catalytic activity from the first member (having seven carbons in the ester group) to the second member of the catalyst series. From the second member of the catalyst series onward, the activity of the compounds levels off.

Comparing the results on the two graphs, it is clear that catalysts with butyl groups are more active than that of the octyl counterpart. It would appear reasonable to explain this difference in reactivity from the two graphs on the basis of the relative shielding power of the ligand bonded to the tin atom in the catalyst. Longer chain alkyl



Figure 1 Effect of length of ligand in organotin carboxylates on its catalytic activity for polycondensation of silicon: (a) dibutyltin (\otimes); (b) diocyltin (\bigcirc).

groups may be considered as having greater power to shield the active center and so to render the catalyst less active and vice versa. Similarly, catalysts with longer ester groups will have greater power to hide the active center of the catalyst and, thus, show a decreased activity and vice versa.

Nagy and Borbely–Kuszmann⁵ also showed that for the two lauroxy catalysts, the one containing a butyl group is more active than the octyl group. However, their graphs do not generalize this observation, and for acetoxy-based catalysts, the reverse trend has been observed. Values for the relative activity of a few organotin compounds as catalysts for urethane have been reported in the literature.⁷ Unfortunately, these catalysts are so diverse in their structure that it is difficult to make a conclusion concerning their reactivity pattern with respect to different groups bonded to tin.

That the catalytic activity for most of the catalysts in the octyl series levels off seems to suggest that the shielding power of the octyl group bonded to the tin atom suppresses the possible difference in reactivity of the catalysts.

It is interesting to note that the second highest molecular weight member of the octyl group, that is, oct₂Sn (C₇H₁₅COO)₂ has 32 carbons, which is comparable in carbon atoms to but₂Sn(C₁₁H₂₃COO)₂ of the butyl series. Comparing the catalytic activities of butyl series of organotin compounds with octyl series, Graph (a) shows that it is from but₂Sn(C₁₁H₂₃COO)₂ onwards where there is no difference in the catalytic activity of the catalysts. Only the first member of octyl series, which has the number of carbon atoms on the

threshold limit, that is, 30, shows somewhat high catalytic activity. However, for the rest of the butyl series of compounds having a number of carbon atoms more than the threshold limit, there is no noticeable change in the catalytic activity. This means that for compounds having more than 30 carbon atoms, the active center is shielded so much that a further increase in the number of carbon makes little difference in the catalytic activity.

This comparison between octyl and butyl series of organotin compounds in reference to their catalytic activities was made in order to help understand the mechanism of the polycondensation reaction. There are a number of theories as to the nature of the active center of the catalyst during curing of HOPDMS. Some scientists⁸⁻¹² relate the catalytic activity to the tin atom in organotin compounds, while another¹ considers that the hydrolysis product of organotin compounds is the actual catalyst during the polycondensation of silicone. A third group of workers¹³ believe that it is the formation of an intermediate product that is further responsible for vulcanization of HOPDMS.

According to the first approach, with tin being a member of the fifth row of Group IV of the periodic table, apart from having 5s and 5d orbitals, also consists of low-energy 5d orbitals that can be utilized in chemical bonding. It is these orbitals that are postulated for coordination between the tin of the organotin compound and oxygen of the HOPDMS or silicone, which, in turn, are thought to bring about ionization of the crosslinker. The polarization and ionization of these bonds results in condensation of the OH groups of the HOPDMS.

Baranovskaya and her coauthors^{10–12} have studied the kinetics of cold vulcanization of HOPDMS in bulk by solution of $R_2Sn(OCOR')_2$ in tetraethoxy silane. According to them, the reactions have specific induction periods and follow through the formation of an intermediate, which has tin as the atom as an active center. They found that an increase in size of the alkyl group on the organotin catalyst decreases the rate of reaction.

However, according to other investigators,¹⁴ condensation starts as early as the essential components, that is, crosslinker, catalyst, and silicone, are mixed, so there is no induction period for the reaction. The order of reaction with respect to catalyst was quoted as unity. The lack of an induction period and the importance of moisture was observed for the polycondensation of

HOPDMS by the author. However the order with respect to tin catalyst was found to be 0.24^3 and not unity.

If the polycondensation of silicone occurs according to this approach, then the decrease in catalytic activity of organotin compounds with increase in length of the ligand (ester or alkyl) can be explained easily on the basis of the relative shielding power of the group. In this case, the length of the dangling group positively influences the shielding of the tin atom, which is considered as the active center.

The observation by a number of workers^{6,15,16} that polycondensation of silicone in the presence of catalyst takes place only if some water is present leads to the belief that organotin hydroxide is a true catalyst instead of dialkyl tin dicarboxylate. Considering this hydrolysis product to be the actual catalyst, as suggested by Van der Weij,¹ the rate of reaction should increase as observed. In order to drive the reaction forward, the carboxylic acid by-product should eliminate on hydrolysis; and so for the lower molecular weight carboxylic acid (that is, the short alkoxy group on the tin atom), the reaction will proceed in a forward direction and therefore increase in the rate of reaction. The findings¹⁷⁻¹⁹ that mono or diorganotin carboxylates undergo complete or partial hydrolysis, and therefore may activate polycondensation through its hydrolysate, supports Van der Weij's suggested mechanism.

Nagy and Borbely–Kuszmann¹³ believed that the crosslinker and organotin catalyst react with one another to form an intermediate product, which in turn acts as crosslinker. They reacted tetraethoxysilane and dibutyldiacetoxytin at room temperature in a molar ration of 1 : 2 and obtained a white crystalline product.

All these various mechanisms, though, differ from one another in terms of the role and fate of the catalyst but do agree about the way that the crosslinker takes part in the reaction. Whatever the mode of action of catalyst for the polycondensation of HOPDMS may be, it would appear from the present results that the increase in shielding power due to increase in length of ligand on organotin compound decreases the catalytic activity.

CONCLUSIONS

The effect of the chemical nature of a range of catalysts based on different structural groups

bonded to the tin atom have been investigated by VNC. All the organotin compounds used catalyzed the polycondensation of HOPDMS. The length of the carboxylic groups bonded to the tin atom does have a measurable effect on the catalytic properties of the catalysts. The increase in length of ester, as well as alkyl groups bonded to the tin atom, decreases the catalytic activity of the catalysts.

It has been established that as the arithmetic summation of the number of carbon atoms in the alkyl and ester groups increase to a limit of 32, then the difference in the catalytic activity of the various organotin carboxylates is suppressed to a nonmeasurable level by VNC.

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