SHORT COMMUNICATIONS

Siloxanes and Silazanes as Activators for Metathesis Polymerizations

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Since the discovery of the “homogeneous” metathesis polymerization, a wide range of initiators consisting of a transition metal compound and an organometallic alkylating agent, has been used.^{1,2} Most of the times, the initiators are used with an activator. The activators are mainly oxygen-containing compounds such as alcohols, peroxides or water. They may activate the polymerizations when they are in very small amount, but too large quantities deactivate the system.³ Consequently, a rigorous control of the activator concentration with respect to the active species taking part in the polymerization process, is required. This is sometimes difficult to achieve since the number of active species cannot be known precisely and consequently, a good control of the polymerization is a very difficult task. In recent years, a new type of well-defined initiators has been developed with much success.^{3,4} However, these initiators are not easily available.

In the present paper, we wish to report the discovery of a new class of activator, that is the siloxanes and the silazanes. Their use does not seem to be restrained by a concentration factor and polymerizations can be carried out using large amounts. The activators have been tried with various cycloalkene monomers, but we wish to report the results mainly for the bulk metathesis polymerization of cyclooctene,

using $\text{WCl}_6/\text{Sn}(\text{CH}_3)_4$ as the initiator.

EXPERIMENTAL

Materials

Cyclooctene (Eastman Kodak, 99%) was first distilled over calcium hydride, degassed, then distilled under vacuum onto a sodium mirror and kept over until its use.

Cyclopentene (Aldrich, 99%) was purified in the same manner and norbornene (Aldrich, 99%) was used right from a fresh supply without further purification.

Tungsten hexachloride, WCl_6 (Aldrich, 99.9%) was kept under purified argon and was transferred as such into a polymerization ampoule.

Tetramethyltin, $\text{Sn}(\text{CH}_3)_4$ (Aldrich, 99%) was kept over a molecular sieve under purified argon. It was degassed prior to its use and distilled into the polymerization ampoule under vacuum or transferred with a syringe.

All the organosilicon compounds (Aldrich 99%) were used without further purification after being kept under dry argon. The organosilicon compounds used for this study were:

- phenyltriethoxysiloxane (PTEOS)
- 1,1,3,3-tetramethyldisiloxane (TMDS)
- hexamethyldisiloxane (HMDS)
- hexamethylcyclotrisiloxane (HMCTS)
- hexamethyldisilane (HMDSi)

- 1,1,3,3-tetramethyldisilazane (TMDZ)
- hexamethyldisilazane (HMDZ)
- heptamethyldisilazane (HPMDZ)

Polymerizations

Polymerizations could be carried out using high vacuum techniques or under purified argon. All reactants were dried and degassed.

WCl_6 was transferred into a dry ampoule through a side arm and then closed with a septum. $\text{Sn}(\text{CH}_3)_4$ was added with a syringe through the septum. The mixture was cooled, the side arm sealed and removed. The mixture was warmed up to room temperature and allowed to react for about 20 seconds. Then the monomer containing the activator was transferred into the ampoule, cooled down and the ampoule was sealed off. The ampoule was warmed up, shaken in order to ensure homogeneity of the mixture and placed in a thermoregulated bath set at the desired temperature.

The polymerization was stopped by the addition of methanol. The polymer samples were analyzed through NMR, size exclusion chromatography (SEC), and mass spectrometry. The samples were made of high-molecular-weight unsaturated linear polymer and unsaturated oligomers in the case of cyclooctene.

RESULTS

The Bulk Polymerization with HMDS

Figure 1 shows the degree of conversion plotted against time for the polymerization of 3 g of cyclooctene using 10 mg of WCl_6 at 45°C. The molar composition of the initiator system $\text{WCl}_6/\text{Sn}(\text{CH}_3)_3/\text{HMDS}$ was 1 : 2 : 4.7. As can be seen, a 50% conversion is reached within 5 minutes. The % conversion levelled off at about 80% due to the formation of a gel.

The same polymerization was carried out at 103°C and 157°C. At these temperatures, the % conversion reached almost 100%. After 3 minutes, the degree of conversion

was approximately 65% at 103°C and 80% at 157°C.

In a set of experiments at 103°C, the HMDS/ WCl_6 ratio was allowed to vary and the time required to obtain maximum conversion, measured accordingly. For a time of 1400 h, the maximum conversion is 85% ($\pm 5\%$) and 95% ($\pm 3\%$) in all other cases. The results are plotted in Figure 2 and they clearly show that an increase of the HMDS/ WCl_6 ratio, increases the rate of polymerization but it has little effect on the maximum conversion. The HMDS/ WCl_6 ratio corresponding to a time of 1400 h is about 0.01.⁵

Figure 1. The variation of % conversion with time for the bulk polymerization of cyclooctene at 45°C using HMDS as the activator.

Figure 2. $\ln t$ against the HMDS/ WCl_6 ratios, t being the time required for the polymerization to reach maximum conversion.

As a matter of fact, we found that in a very clean system (absence of O_2 , H_2O , and any activator) high-molecular-weight unsaturated linear polymers are not formed. This observation is consistent with the remark of Breslow who reported that for another type of metathesis polymerization, "the more careful we were to exclude oxygen and moisture, the poorer yield became"³.

For the $WCl_6/Sn(CH_3)_6/HMDS$ initiator system, the molar masses of the polymer varied from 10^4 to 10^6 g mol^{-1} . As a general trend, the average molar mass has been observed to decrease with an increasing value of the $HMDS/WCl_6$ ratio. Due to the presence of oligomers, the heterogeneity index of the samples were found to range from 2 to 7.

It should be pointed out that at high temperatures (100°C and above), without tetramethyltin, the polymer samples contain a large fraction of saturated and unsaturated oligomers. The proportion of saturated polycyclic oligomers may reach about 80% in some cases for a 50% polymer yield.

The Bulk Polymerization with Various Activators

The bulk polymerization of cyclooctene was carried out between 100°C and 115°C using the organosilicon compounds activators listed above in order to compare their efficiency. In all cases, the molar composition of the catalyst system $WCl_6/Sn(CH_3)_4/\text{accelerator}$ was 1 : 2 : 5.

Table I. Yield after 8 hours for various activators for the bulk polymerization of cyclooctene

Activator	Yield/%
TMDS	100
HMCTS	88
PTEOS	67
HMDS	65
HMDZ	35
TMDZ	35
HPMDZ	Inactive
HMDSi	Inactive

Each activator has its own behavior. In some case, a high degree of conversion can be attained very rapidly but because of a rapid deactivation of the system, the maximum possible degree of conversion will not be reached.

For the sake of comparison, the % conversion was measured arbitrarily after eight hours. The results are presented in Table I. Based on these results, the following qualitative efficiency scale was obtained:

As it is apparent, the presence of methyl group on the nitrogen in heptamethyldisilazane inactivates the compound. The absence of a Si-O bond in hexamethyldisilane has also the same effect. Thus, a Si-O or a Si-NH-Si bond must be present in order to form an activator, the siloxanes being more efficient than the silazanes.

The efficiency scale given here cannot be extrapolated to other monomers, not even to the same monomer at a different temperature in a solvent. More needs to be known about the mechanism before venturing in any kind of generalization regarding this specific aspect of this class of activators.

Polymerization of Other Monomers in Solution

For the sake of comparison, polymerizations of norbornene and cyclopentene in solution were carried out using the catalyst system $WCl_6/Sn(CH_3)_4/HMDS$.

The norbornene polymerization was performed in cyclohexane at room temperature. The catalyst molar composition was 1 : 2 : 4.7. The monomer concentration was 1.88 g in 10.0 ml of cyclohexane with an amount of 10 mg of WCl_6 . The % conversion reached 95% in approximately two minutes. No oligomers were found and the molecular weight of the polymer was about 10^6 .

The polymerization of cyclopentene was carried out in benzene at 0°C . The catalyst molar composition was 1 : 2 : 2.3. The monomer

concentration was 33% and the WCl_6 concentration was 10 mg in a 6 ml monomer-solvent mixture. Because of a monomer-polymer equilibrium in this system, the polymerization never reached completion. It is known that for this polymerization at 0°C , the maximum yield is 70% conversion. In the present case, this was easily achieved within 24 hours. No oligomers were found and the molecular weight of the polymer was about 10^6 .

CONCLUSION

Preliminary results of metathesis polymerizations of various monomers, show that organosilicon compounds, such as siloxanes and silazanes, can be used as activators for this type of polymerization. The results are quite reproducible with temperature but vary de-

pending on the nature of the activator and an activator efficiency scale can be built for a given monomer at given temperature and solvent. Further studies are in progress.

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