

Anionic Polymerization of Cyclosiloxanes in Heterogeneous Medium

MARIA CAZACU,* MIHAI MARCU, STELA DRĂGAN, and CARMEN MATRICALĂ

"Petru Poni" Institute of Macromolecular Chemistry, Aleea Grigore Ghica Vodă Nr. 41 A, 6600 Iași, România

SYNOPSIS

Anionic polymerization of various cyclosiloxanes [octamethylcyclotetrasiloxane (D_4), 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (V_4), and hexamethylcyclotrisiloxane (D_3)] was performed. As catalysts, IRA-900 and PB-100 type anionites with benzyltrimethylammonium and 3-acrylamidopropylbenzyltrimethylammonium groups, respectively, were used. The anionite with higher strongly basic exchange capacity (IRA-900) is more efficient in dimethylcyclosiloxane polymerization. PB-100 anionite with less strongly basic capacity is more active for polymerization of the V_4 monomer with bulky and electronegative substituent. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The catalytic properties of ion exchangers have been known since 1946, but only in the last 25 years have thorough studies been devoted to this field. Besides hydrolysis, hydration, elimination, esterification, and condensation reactions, ion exchangers with catalytic activity have been also used for the analysis and purification of different organic compounds in biochemical synthesis.¹

Utilization of ion exchangers as catalysts in polymerization processes has the advantage of obtaining polymers free of catalyst by simple filtration.² Such polymerizations of vinylic monomers³ and acetic aldehyde^{4,5} have already been performed.

Data on cyclosiloxane polymerization with ion exchangers are scarce and most of them refer to the cationic polymerization,⁶⁻¹¹ essentially with sulfonic cationites, found to be more active than the cationites containing phosphoric or carboxylic groups.⁴

Utilization of anionites in siloxanic ring polymerization is even less known.¹² Djalilov and Niazova³ accomplished the polymerization of vinylic monomers in the presence of crosslinked polymers with ammonium quaternary salt groups. The reaction mechanism involved in this case is radicalic,

and it was confirmed by the reaction inhibition in the presence of hydroquinone or CuCl. The behavior of anionites as catalysts has been studied less because most of the catalytic reactions occur at high temperatures and the anionites' thermal stability is low. During catalytic reactions, even in mild conditions of temperature,¹ they lose their active groups.

Because cyclosiloxanes polymerize easily enough (no excessively high temperatures being required), the present work discusses the utilization of anionites, in OH^- form, for polymerizing siloxanic rings that, as known,¹³ occurs exclusively by ionic mechanism due to the polar character of the Si—O bond. The OCH_3^- form was also tested, but we were unable to provide reproducible results.

EXPERIMENTAL

Materials

Octamethylcyclotetrasiloxane, $|(\text{CH}_3)_2\text{SiO}|_4$ (D_4), 99% purity, with $n_D^{20} = 1.3960$ and $d_4^{20} = 0.9593$ was obtained by hydrolysis of dimethyldichlorosilane, followed by distillation on a Vigreux column. Hexamethylcyclotrisiloxane, $|(\text{CH}_3)_2\text{SiO}|_3$ (D_3), 95% purity, was supplied by ABCR GmbH & Co. 1,3,5,7-Tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane, $|(\text{C}_2\text{H}_3)\text{CH}_2\text{SiO}|_4$ (V_4), 99.1% purity, with $n_D^{20} = 1.4342$ and $d_4^{20} = 0.9892$ was prepared.¹⁴ Am-

* To whom correspondence should be addressed.

berlite IRA-900, supplied by Rohn and Haas, is a macroporous strongly basic ion exchanger, with benzyltrimethylammonium groups in the Cl^- form. PB-100, a macroporous anion exchanger with 3-acrylamidopropylbenzyl dimethylammonium groups in Cl^- form, was synthesized.¹⁵

The characteristics of the two anionites are presented in Table I.

Catalyst Conditioning

The anionite was turned into the OH^- form by treatment with 4% NaOH solution at 30–40°C. Then it was treated with a 4% HCl solution and turned again into the OH^- form, on an installation protected from direct contact with the atmosphere for avoiding carbonation. After each operation the catalyst was washed to neutrality with distilled water, freshly boiled and cooled. The water was removed from the anionite by azeotrope distillation with benzene and then the anionite was dried at 60°C and 15–20 mmHg, until constant weight.

The anionites employed in such investigations were thermogravimetrically analyzed. It was found that over the temperature range in which polymerization occurs, the PB-100 anionite is a little more stable than the IRA-900 one (Fig. 1).

Procedure

Polymerization of siloxane rings took place in a thermostated flask equipped with reflux condenser, thermometer, mechanical stirrer, and pure dry nitrogen inlet.

In the reaction vessel, the required amounts of monomer and catalyst were introduced. For the catalyst's separation, the reaction was stopped by rapid

Table I Characteristics of Anion Exchanger Catalysts Used for Cyclosiloxanes Polymerization

Characteristic	Anion Exchanger	
	IRA-900	PB-100
Apparent density, g/cm^3	0.828	0.729
Exchange capacity:		
C_{vp} , meq/mL	0.753	0.308
C_{vs} , meq/mL	0.062	0.086
C_{vt} , meq/mL	0.815	0.394
C_g , meq/g	3.044	1.721

C_{vp} , strongly basic volumic exchange capacity; C_{vs} , weakly basic volumic exchange capacity; C_{vt} , total volumic exchange capacity; and C_g , total gravimetric exchange capacity.

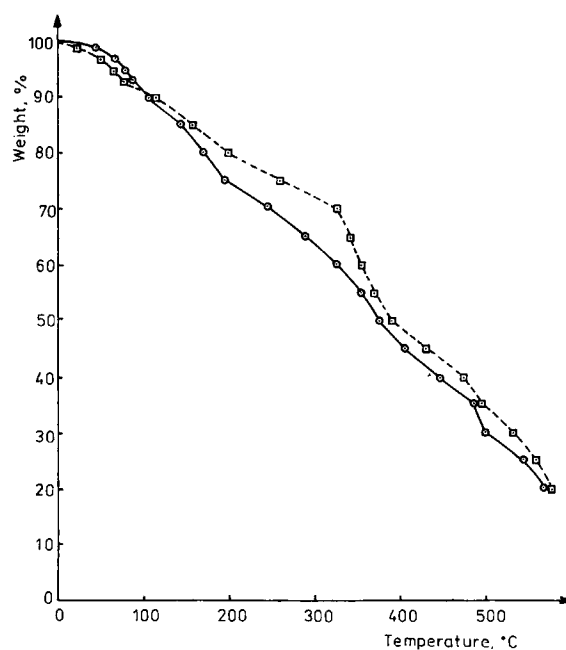


Figure 1 TGA thermograms of the two anionites in OH^- form: (---) for IRA-900 and (—) for PB-100.

filtration of the reaction mixture; the polymer was separated from the unreacted monomer by precipitation with methanol from a toluene solution. The polymer was dried in a vacuum at 100°C until constant weight.

Conversion grade, molecular weight, and molecular weight distribution were studied. Molecular weight and molecular weight distribution were determined by the GPC technique, using a Waters/milipore 244 apparatus with the following characteristics: detector, spectrophotometer UV at 254-nm wavelength; columns, microstyrigel $\cdot 10^5$, 10^3 , 500, 100 Å; eluent, tetrahydrofuran; elution rate, 1 mL/min; sample concentration, 0.5% in tetrahydrofuran; sample volume, 50 μL ; standardization, monodisperse polystyrene (Waters Associates).

RESULTS AND DISCUSSION

The results obtained for siloxanic rings polymerization employing two strongly basic anionites are presented in Table II. As seen in the table, good conversion values were obtained for not too high reaction times. Molecular weight values are low, limited by the relatively high amount of catalyst used for obtaining good conversions. Molecular weight distributions are comparable with

Table II Conversion Degree, Molecular Weight, and Molecular Weight Distribution Data of Cyclosiloxane Polymerization with Strongly Basic Anionites

Sample	Monomer	Catalyst Type	Time (h)	Temperature (°C)	Catalyst Amount (wt %)	Conversion (%)	\bar{M}_n	\bar{M}_w	MWD = \bar{M}_w/\bar{M}_n
A ₄₃	D ₄	IRA-900	2.0	90	1.5	21.27	—	—	—
A ₅₆			4.0	90	1.5	40.00	—	—	—
A ₃₈			6.0	90	1.5	48.33	11,870	20,135	1.696
A ₃₃		PB-100	2.0	90	1.5	9.18	—	—	—
A ₃₂			4.0	90	1.5	24.86	—	—	—
A ₃₁			6.0	90	1.5	38.01	7,815	9,850	1.261
A ₃₄		IRA-900	8.0	90	1.5	46.81	12,716	16,420	1.291
A ₄₅			1.0	90	1.5	20.12	—	—	—
A ₃₉			2.5	90	1.5	51.93	—	—	—
A ₄₀		PB-100	4.0	90	1.5	61.82	—	—	—
A ₄₄			6.0	90	1.5	72.47	—	—	—
A ₃₇			0.5	90	1.5	28.92	18,370	32,210	1.750
A ₃₅		IRA-900	1.0	90	1.5	51.37	19,700	32,350	1.640
A ₂₇			2.0	90	1.5	70.04	18,040	30,710	1.703
A ₃₆			3.0	90	1.5	73.18	21,990	39,860	1.813
A ₃₀		PB-100	4.0	90	1.5	78.00	—	—	—
A ₂₉			6.0	90	1.5	80.33	24,370	40,050	1.643
A ₄₆			1.0	90	0.5	29.50	—	—	—
A ₂₃	D ₃	PB-100	2.0	90	0.5	45.72	—	—	—
A ₂₄			4.0	90	0.5	63.81	—	—	—
A ₄₇			6.0	90	0.5	75.01	—	—	—
A ₄₈		IRA-900	2.0	50	2.5	14.93	—	—	—
A ₁₉			2.0	70	2.5	61.51	—	—	—
A ₁₅			2.0	90	2.5	76.44	—	—	—

D₄, octamethylcyclotetrasiloxane, |(CH₃)₂SiO|₄; V₄, 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane, |(C₂H₃)CH₃SiO|₄; D₃, hexamethylcyclotetrasiloxane, |(CH₃)₂SiO|₃; IRA-900, strongly basic anion exchanger with benzyltrimethylammonium groups; and PB-100, strongly basic anion exchanger with 3-acrylamidopropylbenzylidimethylammonium groups.

those obtained in heterogeneous cationic polymerization of cyclosiloxanes. Study of the variation of conversion grade versus time for D₄ and V₄ monomers, in the presence of the two anionites (Fig. 2) evidences that, while in the case of the D₄ monomer IRA-900 is more active, for V₄ monomer, it is PB-100 that is seen as more active.

Such a behavior may be explained by the conclusions of the study on some organic chemistry reactions in the presence of ion exchangers.^{16,17} According to these reactions, the rate constant increases to a maximum value, for a certain value of the exchange capacity, and then decreases as a result of the diffusion's diminution. Due to this phenomenon, the simple correlations observed between the reaction rate and the amount of catalyst in the homogeneous acid-base catalysis are not the same when employing ion-exchangers.¹

In the case of the D₄ monomer, with increasing the exchange capacity in the working range, from

1.7 meq/g for PB-100 to 3.0 meq/g for IRA-900, the conversion degree for the same reaction time increases too. Because it is bulkier than D₄, increase of the exchange capacity has a reverse effect for the V₄ monomer. That could be explained by the greater porosity of the PB-100 anionite, which favors the diffusion of the bulkiest monomer.

The variation of the D₃ monomer conversion versus time, it is seen as much more marked than that of the D₄ monomer, even for smaller amounts of catalyst (0.5% PB-100), which is certainly due to trisiloxane ring straining.

After the PB-100 anionite's separation from the reaction mixture, its exchange capacity was determined: $C_{vp} = 0.137$ meq/mL, $C_{vs} = 0.220$ meq/mL, $C_{vt} = 0.357$ meq/mL, and $C_g = 1.652$ meq/g. So we found that the strongly basic exchange capacity (C_{vp}) decreases while the weakly basic one (C_{vs}) increases, comparatively with the initial values (Table I), as a result of the partial decomposition of the strongly basic groups, according to the reaction¹⁷:

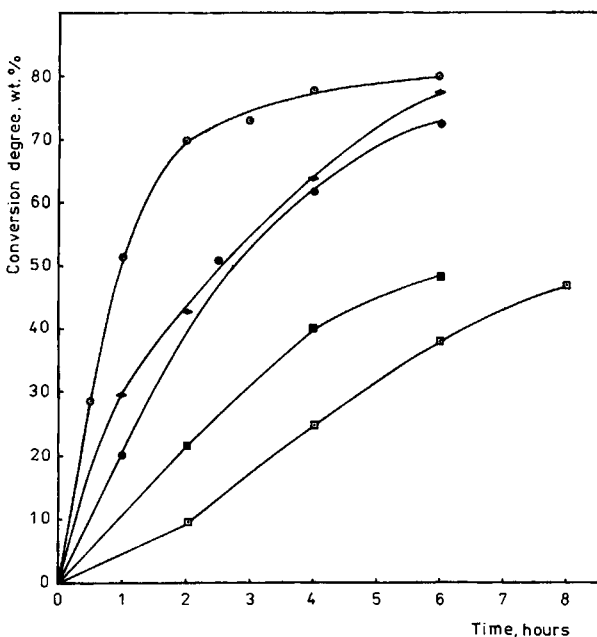
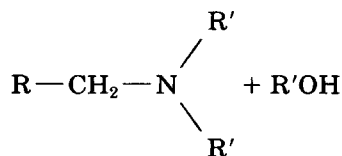
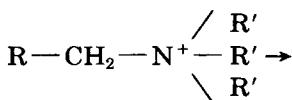


Figure 2 Variation of the conversion degree versus time ($T = 90^{\circ}\text{C}$) in the polymerization of: (\odot) V_4 monomer using 1.5 wt % PB-100 as catalyst; (\bullet) V_4 monomer using 1.5 wt % IRA-900 as catalyst; (\blacklozenge) D_3 monomer using 0.5 wt % PB-100 as catalyst; (\blacksquare) D_4 monomer using 1.5 wt % IRA-900 as catalyst; and (\square) D_4 monomer using 1.5 wt % PB-100 as catalyst.



where $\text{R}'\text{OH}$ is CH_3OH in the case of IRA-900, and $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ in the case of PB-100.

Transformation of strongly basic ammonium quaternary groups into weakly basic tertiary amino ones, the solvation of which is lower, induces an abrupt decrease of the swelling capacity. As a result of this modification, the catalyst activity decreases.¹⁷ For checking such a behavior, the anionite separated from a polymerization mixture was used in subsequent polymerizations under similar conditions, a significant decrease of the conversion grade being noticed from 78 to 23% for the same reaction time.

Polymerizations of the D_3 monomer with PB-100 anionite at three temperatures were performed. It was found (Table II) that the conversion grade increases along with the increase of temperature, for

the same reaction time, which can be explained by the fact that the anionite's decomposition is slower on the initiation of D_3 monomer polymerization.

CONCLUSIONS

Anionites can be applied with good performance in the polymerization of strained (D_3) and unstrained (D_4) siloxanic rings, but preferentially for siloxanic rings with electronegative substituents at the silicon atom (V_4) in mild temperature conditions ($50\text{--}90^{\circ}\text{C}$) and pure inert gas atmosphere.

Utilization of anionites requires higher restrictions than of cationites as to the superior limit of temperature and of the influence of impurities (water, CO_2).

From any other point of view, anionites offer the same advantages as cationites do (easy to separate, stability of the obtained polymer).

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