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Monomer recycling for vulcanized silicone rubbers in the form of cyclosiloxane monomers. Role of acid buffers

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Abstract

The KOH-catalyzed depolymerization of vulcanized silicone rubbers to reproduce cyclosiloxane monomers was studied. First, the depolymerization was carried out in toluene with varying amounts of KOH to find that the yield of monomers first increased and then decreased with the increment of KOH, the highest yield was 65% at the molar ratio KOH/(Si–O) units = 0.08. At the molar ratio 0.13 in the absence of solvent, the monomers yield was 46%. However, when an acid buffer such as KH_2PO_4 and $KCOOC_6H_4COOH$ was added after the KOH-catalyzed depolymerization was over, the product yield was increased remarkably to more than 80%. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Monomer recycling; Silicone rubber; Buffer acid

1. Introduction

The problem of polymer wastes at both post-manufacturer and post-consumer stages is now an important issue to be solved for the global conservation of environment and carbon resources particularly in conjunction with the protection of petroleum resources from depletion. It can be the primary solution to this problem that polymer wastes are recycled by means of depolymerization to monomers via low-energy processes because monomers can reproduce the same polymers compatible with the original ones. Unfortunately, up to now, those polymers that are industrially recycled via monomers are not so many. Since the worldwide annual production of organosilicon polymers has now reached several million tons and the polymers have caused the same problem of wastes treatment as other conventional plastics do, they should also be recycled repeatedly to the same organosilicon polymers. Although inorganic silicon resource is abundant, the industrial framework for recycling silicone polymers is particularly important because a huge amount of energy and carbon resource are required the production of organosilicon monomers [1].

Poly(dimethysiloxane)s (PDMS) are the most important organosilicon polymers, which are produced mainly from cyclosiloxane monomers such as hexamethylcyclotrisiloxane (D_3) and octamethylcyclotetrasiloxane (D_4) by means of ionic ring-opening polymerization catalyzed by acids or bases [2–4]. It is well known that the polymerization involves a thermodynamic equilibrium between the cyclic monomers and linear polymers [5–7]. Based on this fact, linear PDMS can be depolymerized to cyclosiloxane monomers by removing the monomers continuously from the equilibrium under acid or base catalysis [8–12] and, therefore, recycling methods of cross-linked PDMS wastes (vulcanized silicone rubbers) to cyclosiloxane monomers have been already developed [13–18].

The main problem of recycling vulcanized silicone rubber wastes in the form of monomers is that the rate of depolymerization is very slow owing to the network structure even catalysts are used. One method to facilitate the depolymerization is to perform it at a temperature as high as or more than 300 °C in an inert gas atmosphere [13–15]. The other is the use of solvents [16–18]. However, the latter method, on one hand, is energetically undesirable because it requires a solvent-removing process prior to the recovery of monomers. On the other hand, when a high-boiling solvent is used, it is difficult to remove only the monomers from equilibrated depolymerization mixture and, even after the removal of solvent and some monomers, the

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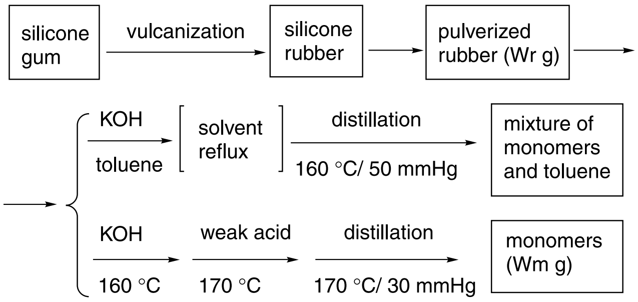


Scheme 1. Experimental procedure for the depolymerization of silicone rubber.

remained PDMS cannot be depolymerized readily to monomers under mild reaction conditions. Consequently, the monomers yields are low. Nevertheless, a fast depolymerization and a high monomers yield are expected to be attained if a high catalyst content is used. Therefore, in this study, the depolymerization of vulcanized silicone rubbers catalyzed by KOH was firstly carried out in toluene and the effect of KOH content on the depolymerization was investigated. The results indicated that the monomers yield did not always increase with the increment of KOH and thus, the highest yield of 65% was obtained at the molar ratio KOH/(Si–O) unit = 0.08. Similarly, in the absence of solvent, the yield was only 46% in the depolymerization carried out at the molar ratio KOH/(Si–O) unit = 0.13. However, we found that the yield can be significantly improved to more than 80% by introducing acid buffers such as KH_2PO_4 and *p*-$KOOCC_6H_4COOH$ to the depolymerization system. In the present report, we describe this result.

2. Experimental

2.1. Materials

Poly(dimethylsiloxane-co-methylvinylsiloxane) gum is commercially available from Dow Corning Co. (SH410), the ratio of vinyl groups to silicon atoms of this gum determined by ^{1}H NMR is 0.02. Vulcanization of the gum was carried out at 170 °C for 10 min after kneaded with 0.8 phr of 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane. Other chemicals KOH, KH_2PO_4, *p*-$KOOCC_6H_4COOH$, P_2O_5, citric acid, toluene, and anhydrous Na_2SO_4 are available from Wako Chemicals Co. Cyclosiloxane monomers D_3, D_4, D_5 and D_6 are commercially available from Shin-Etsu Corp.

2.2. Depolymerization of vulcanized silicone rubber

Vulcanized silicone rubber sheets were pulverized into small pieces having about 1 mm diameters. The rubber pieces, KOH and toluene were added to a 100 ml flask and the mixture was stirred by a magnetic stirrer under heating at the toluene refluxing temperature for 2 h. The formed solution was subjected to distillation at 160 °C/50 mm Hg for 3 h to obtain toluene and monomers. For the depolymerization without solvents, the flask filled with silicone rubber (W_r in grams) and a specified amount of KOH was agitated by a mechanical stirrer for 1 h at 160 °C, then the temperature was raised up to 170 °C, to which KH_2PO_4 or other weak acid was added. Then the reaction mixture was subjected to distillation at 170 °C/30 mm Hg for 2 h, the collected condensate was dried over anhydrous Na_2SO_4 to give the product monomers (W_m in grams). The distillates were collected in a trap cooled at −78 °C. The depolymerization processes are depicted in Scheme 1.

2.3. Characterization

The compositions of monomers were analyzed by gas chromatography on GC-14B (Schimadzu Co.), using commercially available chemicals D_3, D_4, D_5 and D_6 as the standard substances. The conditions of analysis were as follows. Solvent: toluene or acetone; concentration of samples: about 0.05 g/ml; programmed rate of temperature rising: 10 °C/min from 50 to 320 °C; injector and detector temperatures, 320 °C. The yields of monomers in toluene were determined by ^{1}H NMR spectrum recorded at 500 MHz on Bruker DRX-500 using $CDCl_3$ as the solvent. The yields of monomers without solvent were calculated as W_m/W_r (see Section 2.2).

3. Results and discussion

3.1. Depolymerization in toluene

Vulcanized silicone rubber dissolved in toluene very well in the presence of KOH and a clear solution was formed after the dissolution. Because the cross-linking sites of silicone rubber that involves both Si–C and C–C bonds are impossible to be cleaved under this condition, the observed ‘chemical solubilization’ implied that the dissolution was due to depolymerization of PDMS main chains. In other words, the cross-linking network collapsed owing to the breakage of some Si–O bonds of the main chain and the rate of dissolution was controlled by the concentration of KOH under the equilibrium between non-cleaved poly(siloxane)s and cleaved potassium silanolates. The time required for the dissolution decreased clearly by increasing the amount of KOH as shown in Table 1.

The breakage of Si–O bonds by KOH gave silanol groups and potassium silanolates (Scheme 2, Eq. (1)). Cyclosiloxane monomers were formed by back-biting and end-biting processes (Scheme 2, Eqs. (2) and (3)) of potassium silanolates. It is well known that these processes are easily established in equilibria, in which cyclosiloxane monomers (about 10–15 wt%) and potassium silanolate (85–90 wt%) coexist [1]. The amount of cyclosiloxane

Table 1
Effect of the amount of KOH on the solubilization time of silicone rubber and the composition of recycled monomers

Molar ratio KOH/(Si–O unit)	Time for dissolution (min)	Yield of monomers (%)	Product composition[a] (%)				
			D_3	D_4	D_5	D_6	Others
0.028	60	54	13.5	72.3	10.6	0.8	2.8
0.054	30	60	13.6	72.4	9.8	1.3	2.9
0.072	15	67	13.8	71.5	10.4	1.3	3.0
0.109	8	64	13.1	71.5	11.3	1.1	3.0

Silicone rubber: 3.8 g, toluene: 10.6 ml, reaction condition: refluxed for 2 h and then distilled at 160 °C/50 mm Hg for 3 h.

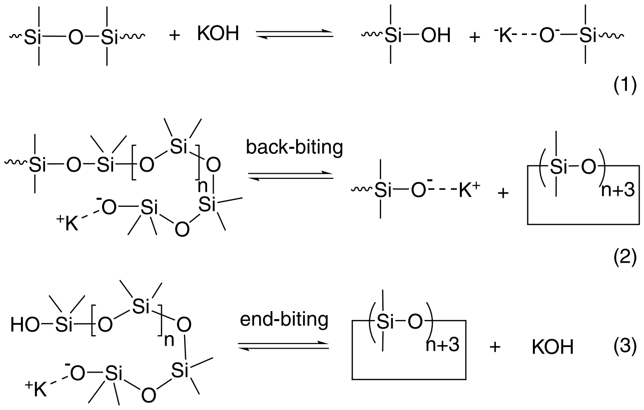
[a] Molar ratios were calculated based on GC analysis.

monomers varies little with the conditions such as catalysts, temperatures and solvents [1,7].

As the volatile fraction containing toluene and monomers was removed, the viscosity of residual materials became higher. With a low KOH content (molar ratio KOH/(Si–O) unit < 0.08), the residue turned into a gel state during the depolymerization. This is because the potassium silanolates reacted again with silanol groups to form Si–O–Si bonds, thus reconstructing a network. Once the gel state was formed, the depolymerization became imperceptibly slow owing to the poor mobility of the PDMS chains. The relationship between the yield of monomers and KOH content is shown in Fig. 1, where one can see that the yield first increased and then decreased with the increment of KOH, the highest yield was about 65% obtained at the molar ratio KOH/(Si–O) unit $= 0.08$. The first increase in the yield at a low KOH content was easily understood in terms of catalytic rate acceleration by KOH. The reason for decreasing yield with the increment of KOH can probably be explained as follows.

Starting with potassium silanolate possessing a short chain (for example, three to six Si–O units), cyclic monomers can be produced mainly by end-biting process (Scheme 2, Eq. (3)). There are two types of potassium silanolates, i.e. single-potassium silanolate ($KO-[Si(R)_2-O]_n-R'$) and dipotassium disilanolate ($KO-[Si(R)_2O]_n-OK$). Apparently, the end-biting reaction of dipotassium disilanolate is more difficult than single-potassium silanolate because silicon atom of Si–OK is much less electrophilic than that of Si–OH, and also more difficult than a back-biting process for the same reason. Thus, under the conditions of high temperatures and low pressures, dipotassium disilanolates dominate because silanol groups cannot exist in the presence of KOH. In addition, with a high KOH content, the chain length of dipotassium disilanolates becomes short and consequently, the rate of depolymerization becomes slow. More, dipotassium disilanolates of one or two Si–O units cannot produce the monomers and, consequently, the yield of monomers decreased with the increase of KOH content. This is a rational reasoning for the poor monomers yield. Poor mobility of the PDMS chains, as was suspected by the observation of a viscous state at high temperature (170 °C) and a gel state at a room temperature with a high KOH content (molar ratio KOH/(Si–O) unit > 0.8), may not be an attributable reason.

To estimate the effect of chain mobility on the monomers yield, the depolymerization was repeated two or three times. Using a low KOH content, the depolymerization was first carried out four times, but the fourth one did not product the monomers suggesting that three repetition was enough to obtain the highest yield. All the monomers yields, i.e. of second and third depolymerization and combined yields of



Scheme 2. Depolymerization mechanism of polysiloxane ($n \geq 0$).

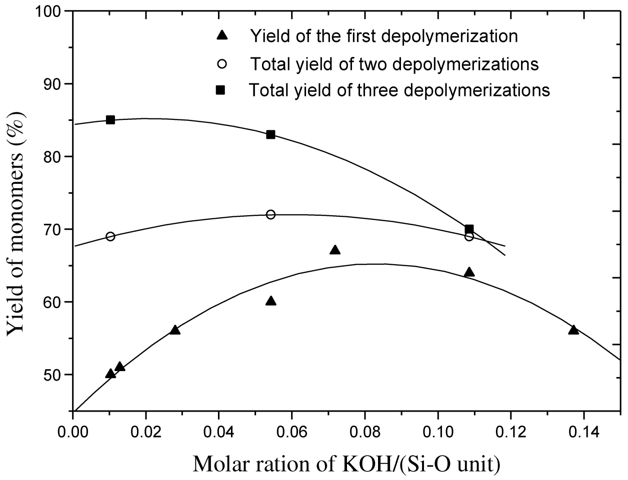


Fig. 1. Relationship between the amount of KOH and monomers yield. Silicone rubber 3.8 g, toluene 10.6 ml for the first depolymerization, additional 4.5 ml of toluene for each of the second and third depolymerization were used. Reaction mixtures were heated under solvent reflux for 2 h and then distilled at 160 °C/50 mm Hg for 3 h.

Table 2
Effect of buffer acid on the yield of recycled monomers

Entry	Buffer acid[a]	Molar ratio: buffer acid/KOH	Yield of monomers (%)
1	–	–	46
2	KH_2PO_4	1.0	83
3	p-$KO_2C(C_6H_4)CO_2H$	1.0	84
4	P_2O_5	0.25	69
5	Citric acid	0.33	64

In each entry, amount of silicone rubber specimen: 7.0 g; molar ratio KOH/(Si–O) unit: 0.13; reaction conditions: 160 °C for 1 h and then distilled at 170 °C/30 mm Hg for 2 h.

[a] Added before distillation.

three depolymerizations, decreased with increment of KOH content as shown in Fig. 1.

The monomers products, namely recycled monomers, were found to contain mainly D_3, D_4, decamethyl-(D_5) and a little amount of dodecamethyl analogue (D_6) by gas chromatographic analysis (Table 1). In Table 1, product 'others' was assigned to a mixture of larger cyclosiloxanes and those containing vinyl groups as was proven by ^1H NMR. The latter would have come from incomplete vulcanization. Table 1 also shows that the amount of KOH has no obvious effect on the composition of recycled monomers.

3.2. Depolymerization in the absence of solvent followed by the addition of buffer acids

On the basis of above-described experimental results that were not satisfactory as we expected in the beginning, a few novel ideas evolved in our program. They were: (1) abbreviation of solvent and the use of a high KOH content in the depolymerization, (2) gradual addition of an acid to the reaction mixture of potassium silanolates at an intermediate stage of the depolymerization to obtain monomers in high yields. The reason for (2) is that after the cleavage of PDMS reaches an equilibrium stage, gradual addition of an acid will neutralize an excess amount of dipotassium disilanolates to transform them into single-potassium silanolates and, consequently, reduce the amount of smaller potassium silanolates being composed of one or two Si–O units that are otherwise difficult to form cyclic structures. However, the control of this acid addition was not so easy. A substitute for this method was the employment of buffer acids, which can be added to the depolymerization mixture at a certain stage of depolymerization to neutralize potassium silanolates and keep the concentration of silanolates at a low level.

Indeed, the idea of adding buffer acids to the reaction mixture in the midway of depolymerization was found successful. In the first experiment, a mixture of vulcanized silicone rubber and KOH with the molar ratio KOH/(Si–O) unit = 0.13 was heated under a mechanical stirring at 160 °C for 1 h to form a viscous liquid mixture, which was then subjected to distillation in vacuo to afford monomers in 46% yield. In the second experiment, after the depolymerization with KOH was over as described above for the first experiment but before the reaction mixture was subjected to distillation, one of such weak acids as KH_2PO_4, p-$KOOC(C_6H_4)COOH$, P_2O_5 or citric acid was added, at most up to the same molar equivalence as KOH, and then the mixture was subjected to distillation. Table 2 shows the effect of addition of buffer acids on the yields of recycled monomers, and all these acids were found more or less effective to raise the yields. Among them, of particular, KH_2PO_4 and $KCOOC_6H_4COOH$ were more effective than the others. It was also noted that with any acid, the composition of product monomers varied little from those listed in Table 1.

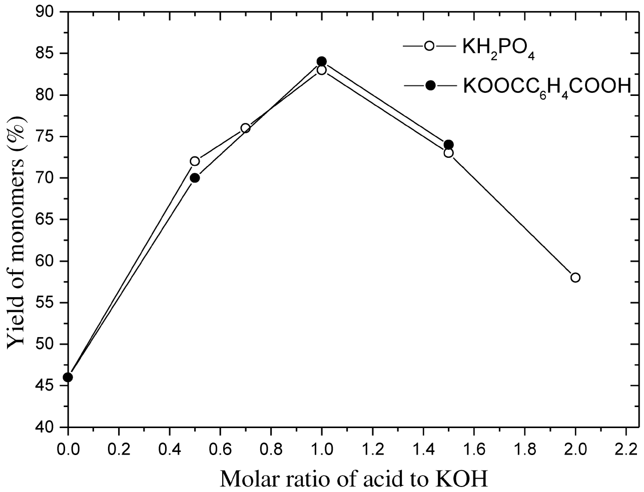


Fig. 2. Effect of the amount of buffer acids on monomers yield.

Obviously, the effect of such buffer acids depends on their controlled acidity. Too-strong or too-weak acidity is not effective. With a too-weak acid, the potassium silanolates are not neutralized effectively, whereas with too-strong acid, the content of KOH becomes too low not sufficient to the depolymerization. In this regard, both KH_2PO_4 and p-$KOOC(C_6H_4)COOH$ have weak acidities and are solids with melting points higher than the reaction temperature, thus shifting the equilibrium point of neutralization to a moderately acidic position. In analogous comparison, diphosphorus pentaoxide (P_2O_5) has an acidity much stronger than the above-described buffer acids, and citric acid has a low melting point (153 °C) as well as instability under the reaction temperature.

The effect of the amount of buffer acids on the yield was studied and results are depicted in Fig. 2. The relationship between monomers yields and molar ratio of buffer acid to KOH was almost the same with both KH_2PO_4 and p-$KOOC(C_6H_4)COOH$. In the beginning, the yields increased as the molar ratio of acid to KOH increased, and the highest yield was obtained when the ratio reached 1.0. After this stage, as the ratio increased, the yield decreased. Thus, the neutralization of silanolate intermediates plays a significant effect on the efficacy of monomers' recovery.

4. Summary

The KOH-catalyzed depolymerization of high-temperature-vulcanized silicone rubbers into cyclosiloxane monomers was first conducted in toluene solution and the effect of KOH content on the composition and yields of monomers was investigated in detail. The results showed that KOH content has no obvious effect on the composition of monomers but a significant effect on the yields of monomers, first increasing and then decreasing with the increment of KOH to give the highest yield 65% at the molar ratio KOH/(Si–O) unit = 0.08. Inefficacy of monomers yields, however, was improved by adopting a solventless system, in that the depolymerization was first carried out with KOH (molar ratio of KOH/(Si–O) unit = 0.13) to produce potassium silanolates and then, after the addition of buffer acids such as KH_2PO_4 and *p*-$KOOC(C_6H_4)COOH$, the monomers were obtained in much improved yields of 84%.

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