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Production Process and Characteristics of Styrene Oligomers

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Production Process and Characteristics of Styrene Oligomers*



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1 Introduction

The development of low molecular weight styrene oligomers (KSTO) of Kawasaki Steel Corp. results from basic research at the corporation's Chemical Research Center. KSTO is obtained by bulk polymerization of styrene using a perfluorinated ion exchanger, Nafion-H (Du Pont), as a catalyst. The number-average molecular weight (M_N) of KSTO thereby obtained ranges from 250 to 800.

Styrene oligomer was industrially used as an electric conductivity treatment reagent for paper¹⁾ and has been supplied by Sanyo Chemical Industries, Ltd. (Heimer²⁾), and by Dainippon Ink and Chemicals, Inc. (Elastyrene³⁾). However, these oligomers are produced by thermal polymerization or radical polymerization, resulting in a fairly high degree of polymerization, that is from 1000 to several ten thousands in M_N .

We have studied a polymerization process using a solid catalyst for continuous processing and simpler separation of the catalyst from reaction products. As a result, it was found that Nafion-H, a solid super-acid, was very effective in the production of low molecular weight oligomer by cationic bulk polymerization of styrenes and had a long life as a practical catalyst⁴⁾. A continuous reaction equipment with capacity of 10 l/h was installed in July 1987 after several basic experiments.

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Synopsis:

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The technical base is a new application of a solid acid catalyst, Nafion-H supplied by Du Pont, to bulk polymerization of styrenes. The number-average molecular weight of KSTO is between 250 and 800, and the iodine value ranges from 20 to 70. KSTO is clean, faint both in color and odor, and harmless. Owing to its high compatibility with other resins and good dielectric properties, KSTO can be widely used as a modifier of polymers and a UV coating material.

Furthermore, a functional group can be introduced to these oligomers because of their olefinic double bond, and as a result, a new application such as a high performance epoxy resin hardener is expected.

We have produced a few types of styrene oligomer and have begun a study as to the application of these oligomers.

This paper deals with the basic aspects of the production process of KSTO, and characteristics and application of KSTO.

2 Polymerization of Styrenes

2.1 Methods of Polymerization

The following polymerization methods for aromatic vinyl compounds such as styrene have been practiced: thermal polymerization, radical polymerization by the use of initiator, and ionic polymerization (anionic and cationic). A radical polymerization method is widely used as the manufacturing process of polystyrene which is an important commodity polymer. Furthermore, as a special example, it is known that anionic polymerization using an Li catalyst creates a living polymer with a narrow molecular weight distribution⁵⁾.

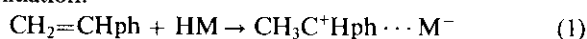
On the other hand, cationic polymerization of styrenes has been widely studied using many types of acid catalysts, but only a linear dimer of α -methyl-

styrene has been commercially produced. The linear dimer was attractive as a raw material of traction oil, and many production processes have been proposed⁶⁻⁸⁾. In the case of styrene, it is known that polystyrene in the oligomer region can also be produced. For example, a selective synthetic method of the unsaturated dimer of styrene by using P₂O₅ as a catalyst⁹⁾, a process using an ion exchange resin¹⁰⁾, a process using a Lewis acid catalyst¹¹⁾, and a process using electron beam¹²⁾ have been proposed. Higashimura et al.^{10,13)} have proposed a process using an ion exchange resin, in which polymerization is conducted in the low concentration of styrene in solvents. In this case, an adduct of styrene and solvent formed besides oligomer depending on the solvent used. Bulk polymerization using a Nafion membrane, as disclosed by our patent, was the first process and is still a very effective method for producing styrene oligomers.

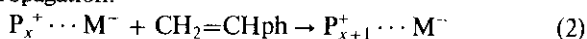
2.2 Cationic Polymerization

Cationic polymerization of styrenes is discussed in detail in the textbook¹⁴⁾ and the review¹⁵⁾ of Higashimura, therefore only the important points, concerning the cause of product distribution and the method for producing oligomers with different molecular weight, are summarized here. The instability of carbonium ions, involving the propagation, and the involvement of counter anions M⁻ in the initiation and propagation, shown in Eqs. (1) and (2), show the reasons why cationic polymerization never produces a high molecular weight polystyrene as is produced by radical polymerization. When a counter anion M⁻ is unstable, it causes the termination of polymerization as is shown in Eq. (3) and leads to deactivation of the catalyst (initiator). This is very important in the case of solid catalysts. Besides Eq. (3), the termination of polymerization is also encountered under Eq. (4), self-transfer reaction (elimination of proton), and Eq. (5), transfer to monomer (cyclization of the end).

Initiation:



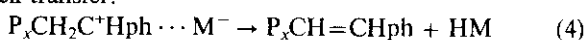
Propagation:



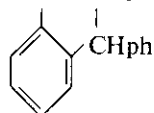
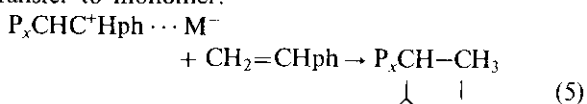
Termination:



Self-transfer:



Transfer to monomer:



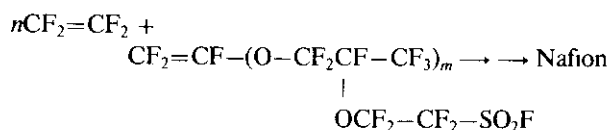
In the above, ph means phenyl group, and P_x⁺ means propagation cation with x monomers.

As is realized by the reaction mechanism mentioned above, the character of counter anion (M⁻) plays an important role in cationic polymerization. The change in character of counter anion, that is the change of catalyst, leads to a different molecular weight and molecular weight distribution of the product obtained by similar protonic catalyst.

The authors have established a production process for low molecular weight styrene oligomer having a different molecular weight distribution and a degree of unsaturation^{16,17)}. The unsaturated dimer and saturated dimer mentioned in the paper are produced according to Eq. (4) and Eq. (5) respectively, and the molecular weight and molecular weight distribution vary according to the degree of propagation under Eq. (2).

3 Nafion as a Catalyst

Nafion is the product name of the perfluoro-polymeric ion-exchanger supplied by Du Pont (USA), and was developed in 1962 by Dr. Grott of the company¹⁸⁾. Initially, it was applied to fuel cells and the like, but now, owing to its heat-resistance and chemicals-resistance, it is being used solely as an ion-exchange membrane for manufacturing sodium hydroxide by electrolysis of sodium chloride. Nafion is a copolymer of perfluoro-ethylene and its derivative shown below.



Film type Nafion N-117 and N-324 (reinforced with fiber) are used as ion-exchange membranes, while granular type one, Nafion-H (NR-50), is now being studied for use as a catalyst. Nafion is a solid super acid which is stronger than 100% sulfuric acid, and has been applied as a solid acid catalyst¹⁹⁾. **Table 1** shows

Table 1 Important industrial reactions

Alkylation	
$\text{C}_6\text{H}_6 + \text{CH}_2=\text{CH}_2 \longrightarrow \text{C}_6\text{H}_5\text{Et}$	
Amination	
$(\text{CH}_3)_2\text{C}=\text{CH}_2 + \text{NH}_3 \longrightarrow (\text{CH}_3)_3\text{CNH}_2$	
Esterification	
$\text{CH}_2=\text{CHCO}_2\text{H} + \text{CH}_3\text{CH}_2\text{OH} \longrightarrow \text{CH}_2=\text{CHCO}_2\text{CH}_2\text{CH}_3 + \text{H}_2\text{O}$	
Etherification	
$(\text{CH}_3)_2\text{C}=\text{CH}_2 + \text{CH}_3\text{OH} \longrightarrow (\text{CH}_3)_3\text{COCH}_3$	
Hydration	
$\text{CH}_3\text{CH}=\text{CH}_2 + \text{H}_2\text{O} \longrightarrow (\text{CH}_3)_2\text{CHOH}$	
Nitration	
$\text{C}_6\text{H}_6 + \text{HNO}_3 \longrightarrow \text{C}_6\text{H}_5\text{NO}_2 + \text{H}_2\text{O}$	
Oligomerization	
$(\text{CH}_3)_2\text{C}=\text{CH}_2 \longrightarrow \text{dimers, trimers and tetramers}$	

examples of important industrial reactions using acid catalysts, and Nafion has been studied as a catalyst in the basic research of each reaction. In this field, G.A. Olah is also a pioneer, and has reported as many basic studies as Du Pont^{20,21}. However, there is no industrial process using Nafion as a catalyst at present and, as far as we know, there are few processes in the real development stage.

4 Summary of KSTO Process

4.1 Basic Experiments

4.1.1 Experimental

(1) Catalysts

There are three types of catalysts used in this work and they are shown in Table 2. These are all copolymer described in chapter 3. N-324 is a film reinforced by fiber, which is mainly used as a membrane for electrolysis to produce sodium hydroxide. NR-50 differs from N-117 in that it is developed as a catalyst and is a granular type.

Nafion-H is exchanged in the form of H⁺, but since a small amount of K⁺ remains, it was pretreated by washing with solvents and by exchanging ions with HCl. In the case of styrene polymerization, the initial activity of the catalysts was not affected by the pretreatment. However, the untreated catalyst was inactive in some types of reaction (e.g. alkylation, aralkylation).

(2) Reaction Conditions

Commercial styrene was used as received for the reaction. It usually contains about 30 ppm of polymerization inhibitor (t-butyl catechol), but it was confirmed that cationic polymerization was not affected by the presence of this inhibitor.

In a batch type reaction, raw material styrene was placed in a flask equipped with a three-way cock (capacity: 300 ml–2 l), with a condenser, a thermometer, and a stirrer, and heated to the reaction temperature, then the reaction was effected for a fixed time after the catalyst was added. Unreacted styrene was separated from the reaction products by distillation. The conversion was estimated based on the weight of reaction products and on gel-permeation chromatography (GPC) or gas chromatography. Gas chromatographic analysis employing an internal standard material is accurate and suitable in order to examine the reaction velocity.

A continuous experiment for determining the life of the catalyst was conducted for 1~2 months by continuously supplying styrene via a plunger pump to continuous reaction equipment with a capacity of about 500 ml.

4.1.2 Analyses

The products were analyzed by GPC. Number-average molecular weight (M_N), weight-average molecular weight (M_W), and molecular weight distribution

Table 2 Catalysts used in the present process

	Nafion-117	Nafion-324	Nafion-NR-50
Type	Membrane	Membrane	Granule
Reinforcement	No	Yes	No
Ionic form	H ⁺	H ⁺	H ⁺
Acid equivalent weight	1 100	1 100	1 100

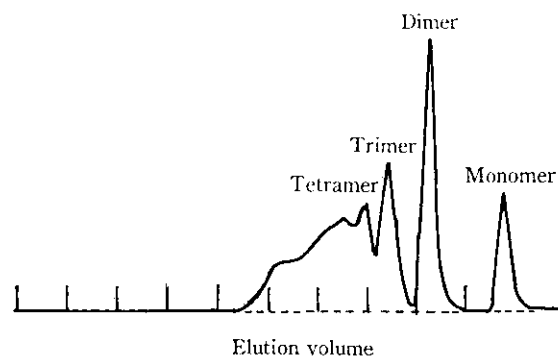


Fig. 1 An example of gel-permeation chromatogram of reaction product

(M_W/M_N) were calculated on the basis of a single dispersed polystyrene calibration. A typical GPC chromatogram example is shown in Fig. 1.

Product constituents with boiling points below 450°C were analyzed by GC with FID. Furthermore, some of the constituents were identified by GC-MS. An iodine value was evaluated by JIS K0070.

From the iodine values and the number-average molecular weight (M_N) estimated by GPC, the degree of unsaturation (D_u), which indicate the number of double bonds in one mole of the product, is calculated according to Eq. (6).

Degree of unsaturation (D_u)

$$= \frac{\text{Iodine value} \times M_N}{253.8 \times 100} \dots \dots (6)$$

4.1.3 Results of reaction

The cationic polymerization of styrene was investigated by varying the reaction conditions, the kind and amount of the catalyst, and the reaction method. As a result, some information was obtained about the conversion of styrene, product characteristics, the life of catalysts, and the choice of a reaction system.

Figure 2 shows the relationships between reaction temperature and conversion or degree of unsaturation of the products. In these reactions, 0.8 wt.% of N-324 was used at 25°C~140°C, and the reaction time was 2 h. The conversion increased almost linearly with the reaction temperature, and reached almost 100% at

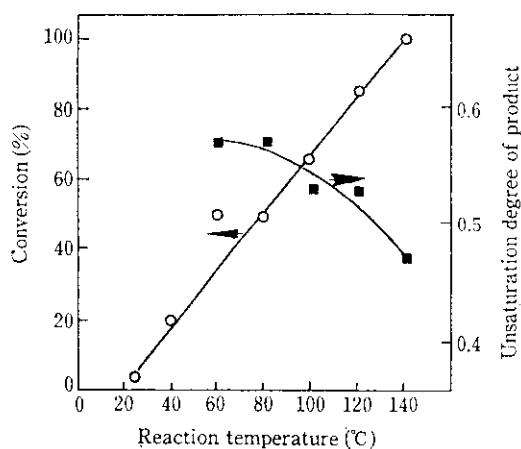


Fig. 2 Relationship between reaction temperature and styrene conversion and unsaturation degree of product in the 2 h reaction with a catalyst of 0.8 wt.% N-324

140°C. The degree of unsaturation evaluated for some products is shown in Fig. 2. It shows that D_u decreases with an increase of reaction temperature. Although not shown in this figure, it was confirmed by GC that the amount of saturated dimer increased with an increase of the reaction temperature. This is due to an increase of ring formation reactions caused by the transfer reaction of monomer (Eq. (5)) at high temperatures.

Figure 3 shows the relationship between reaction temperature and M_N of the products under the same reaction conditions mentioned above. M_N of the product around room temperature was about 600, but decreased gradually with an increase of reaction temperature, and reached about 350 over 120°C. It is recognized that propagation is hindered because the stability of carbenium ion decreases at high temperatures. As was mentioned above, the bulk polymerization of styrene using the film catalyst produces oligomers whose M_N range from 350 to 600 in the absence of a particular additive.

Figure 4 shows the change in product distribution against reaction time at 100°C, with 0.8 wt.% of N-324 catalyst. The changes in existing amount determined by GPC area percentage concerning dimer, trimer, tetramer, and over pentamer against reaction time are shown in this figure. The figure shows that product distribution does not change with reaction time. This result supports a belief that only monomer is activated by a catalyst, while in the presence of excess monomer, unsaturated dimer and trimer formed are rarely activated to take part in the oligomerization process.

In this regard, the authors are now studying the activity of olefinic double bond contained in the styrene oligomer, in the fields of thermal reaction, radical reaction, and ionic reaction. Since the results obtained in these studies are extremely important for considering the modification and the use of the oligomer, the authors

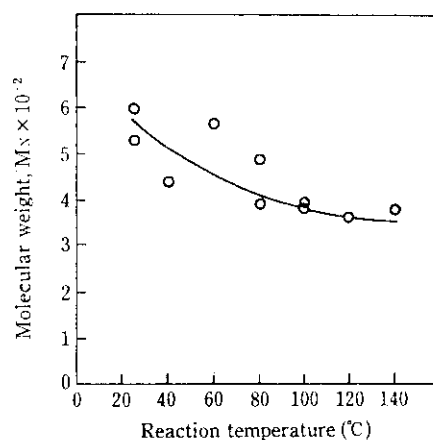


Fig. 3 Effect of reaction temperature on molecular weight (0.8 wt.% N-324 vs styrene; reaction time, 2 h)

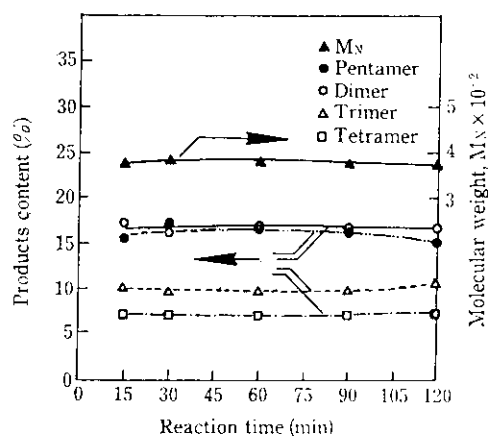


Fig. 4 Effect of reaction time on products distribution and molecular weight (0.8 wt.% N-324 vs styrene; reaction temperature, 100°C)

would like to report the results on another occasion.

Figure 5 shows the change of styrene conversion against reaction time in the presence of 0.3 wt.% granular catalyst NR-50 (15~35 μ) at 40~100°C and 1~4 h. As compared with Fig. 2 and the results of N-117 catalyst, the initial activity of NR-50 is high. However, NR-50 has the problem of being badly worn in a suspension type reactor. Furthermore, the M_N of the oligomer produced with NR-50 is under 1000.

Figure 6 shows the result of a continuous reaction in a small-sized reactor using untreated N-117 catalyst. The initial activity of N-117 was also high in this case, but the conversion of styrene declined greatly with reaction time, and the amount of polystyrene ($M_N > 30000$) formed in this reaction reached several percentage in about 20 days. When a pretreated catalyst was used, it was confirmed that both the conversion of styrene and the product distribution were stable.

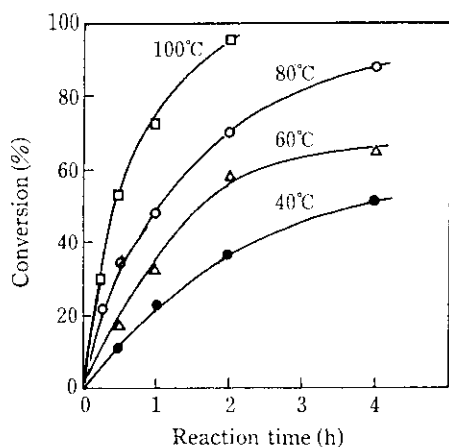


Fig. 5 Effect of reaction time on conversion of styrene (0.3 wt.% NR-50 vs styrene)

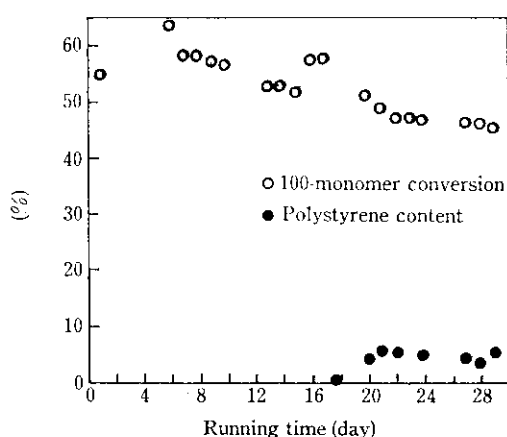


Fig. 6 An example of the continuous reaction at 100°C (0.3 wt.% untreated N-117 vs styrene; residence time, 4.8 h)

4.2 A Summary of a 10 l/h Continuous Reaction Equipment and Examples of Oligomer Production

4.2.1 A summary of the equipment

There has been no precedent showing that styrene

oligomer is produced by continuous bulk polymerization using Nafion. Moreover, no chemical engineering data such as decisions regarding the reaction type and the necessary scaling up for industrialization have been reported. A large sample is required to determine suitable commercial applications. Under these circumstances, the 10 l/h continuous reaction equipment was built in Chiba Works, and its flow diagram is shown in Fig. 7. The major development of the equipment is in the areas of polymerization processes and recovery of the unreacted monomer. A DDC centralized control system was adopted for this equipment, so the entire operation can be performed from the control room except for the starting of pumps, operating the bulbs, and sampling of products.

4.2.2 Examples of production

(1) Paste Oligomer

In a reaction where 0.3 wt.% of a catalyst was used at the reaction temperature of 100°C and the average residence time of 5 h, average conversion was about 65% and the M_N of the product was about 520. The product was named D type.

(2) Liquid Oligomer

As we have already described, molecular weight distribution can be controlled if a certain additive is used as well as styrene and a catalyst. On the basis of this concept, a continuous reaction was carried out at 100°C, 4 h of average residence time in the presence of 0.3 wt.% of the catalyst, and 6 wt.% of the additive. The conversion of styrene and the change in molecular weight against reaction time early in the reaction is shown in Fig. 8. The M_N of the product reached 300 ± 10 and conversion of styrene was about 65% in 20 h. The oligomer produced in this reaction was liquid at room temperature. The fluid point and the iodine value were 10°C and 67, respectively. The product was named E₂ type. E₁ type described in the next section can be produced under similar conditions.

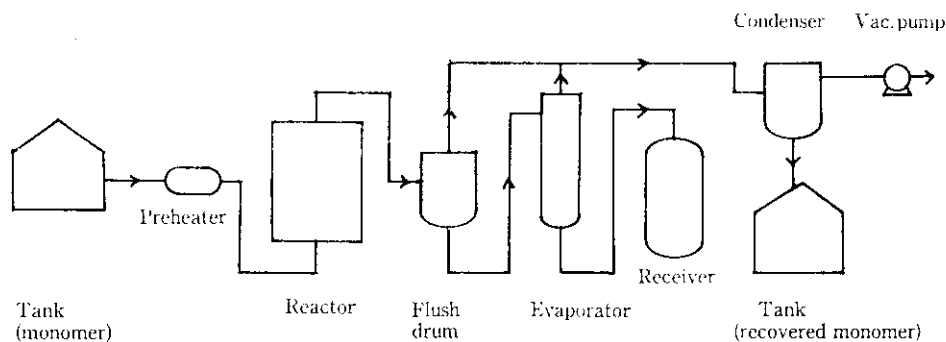


Fig. 7 Block diagram of the 10 l/h continuous reaction equipment

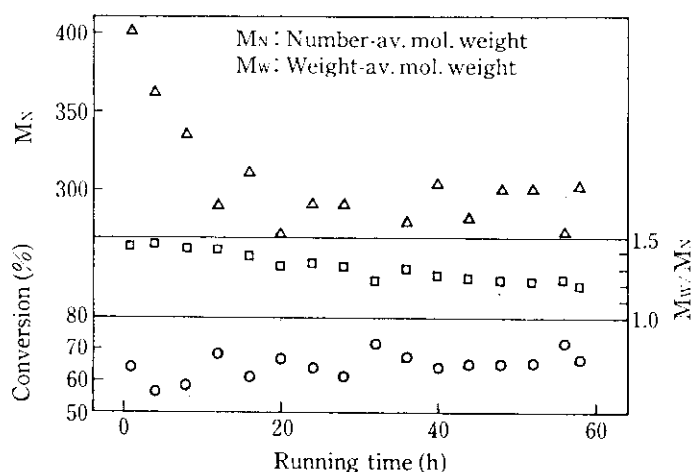


Fig. 8 A result of styrene oligomerization in the continuous reaction equipment (100°C; catalyst, 0.3 wt.%; residence time, 4 h)

5 Features and Characteristics of KSTO

5.1 Features of KSTO

KSTO does not contain impurities such as ionic substances, halides and heavy metals, because it is produced by using Nafion which is a polymeric solid acid catalyst. KSTO is a low molecular weight oligomer, which is clean, has a faint color, almost no odor, and is harmless. In addition, the olefinic double bond of unsaturated constituents contained from 80 to 90% in the oligomer is active to some reactants; therefore it can be used for a variety of modification reactions and curing with high energy rays.

5.2 Characteristics of KSTO and Characterization Method

A variety of characterization methods were applied to KSTO produced in the 10 l/h continuous reaction equipment, and general characteristics of KSTO and the characterization method are shown in Table 3. In a laboratory scale, dozens of grams of oligomers (M_N 600~1000) were produced, while three types of oligomers, D, E₁, and E₂, shown in Table 3, were produced in the continuous reaction equipment to the scale of several hundred kilograms. These oligomers are liquid or paste at room temperature. The iodine value of E₂ type is comparatively high, and it is easily handled because of its liquid form.

Table 3 Characteristics of KSTO and characterization method

		Product			Method
		D	E ₁	E ₂	
Specific gravity	(d_4^{20})	1.030	1.005	1.012	JIS K 2249
Gardner color No.		1	<1	<1	JIS K 5400
Viscosity					
at 100°C	(Poise)	6.5	0.1	0.3	Viscometer
at 25°C	(Poise)	—	3.0	205	
Softening point	(°C)	45	—	—	Ring and ball
M_n^{*1}		520	310	340	GPC
M_w^{*2}/M_n		1.7	1.2	1.3	GPC
Dimer	(%)	12	38	25	GC
Monomer	(%)	0.3	tr.	tr.	GC
Polymer	(%)	1.0+0.5	1.0+0.5	1.0+0.5	GPC
Unsat. dimer/sat. dimer		81/19	86/14	88/12	GC
Iodine value		34	62	67	JIS K 0070
Acid value		0.05	0.01	0.05	JIS K 0070

* M_n : Number-average molecular weight

* M_w : Weight-average molecular weight

Table 4 Dielectric properties of KSTO

	E ₁	E ₂
Dielectric constant at 20°C	2.7	2.6
Dielectric loss at 20°C (%)	0.16	0.026
Volume resistivity at 20°C (Ωcm)	5.7 × 10 ¹²	1.8 × 10 ¹⁵
Dielectric strength at 25°C (kV)	65	42

In addition to the general characteristics of KSTO, dielectric properties, compatibility with other resins, solubility with several solvents, and thermal stability of KSTO were also measured. The dielectric properties of KSTO are shown in Table 4. The volume resistivity of E₁ is low because E₁ contains a small quantity adduct between styrene and the additive, while the dielectric properties of styrene oligomer itself are excellent, like E₂.

6 Expected Use of KSTO

KSTO is a low molecular weight styrene oligomer. Because of its good compatibility with other resins and its high reactivity with olefinic compounds having electron-withdrawing groups, the following applications are expected:

- (1) Modifier of resins
- (2) Additive to unsaturated polyester for lower shrinkage (prevention of cracks)
- (3) Modifier or hardener (modified oligomer) of epoxy resin
- (4) Plasticizer, additive for improving fluidity
- (5) Coating materials
- (6) Vehicle of ink and paint
- (7) Curing by high energy rays (improvement of adhesion)
- (8) Dielectric materials

Moreover, various derivatives of KSTO could be produced based on the reactivity of the low molecular weight oligomer. Some applications of the oligomer and the modified oligomer are presently being carried out in our research center²²⁻²⁴.

7 Closing Remarks

The important points of the production process of the low molecular weight styrene oligomer and its general characteristics are summarized as follows:

- (1) Low molecular weight styrene oligomer can be effectively obtained by bulk polymerization using a

solid super acid, Nafion, as a catalyst.

- (2) Several kinds of styrene oligomer with different molecular weight and degree of unsaturation are produced with a good reproducibility by experiments in the 10 l/h continuous reaction equipment.
- (3) The number-average molecular weight of the oligomer obtained in the experiments was in the several hundreds, and the oligomer comprised about 85 percent unsaturated compounds.
- (4) The main uses of the oligomer are as resin modifiers, coatings, dielectric materials, and curing composition by energy rays.

As was described above, Kawasaki Steel has developed the first bulk polymerization process for producing styrene oligomer by using the solid acid catalyst, Nafion. Although this paper treats a case of styrene as a representative of all styrenes, the process can be applied to other styrenes such as α -methylstyrene and p-methylstyrene. The authors would like to introduce a few examples of such uses on another occasion.

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