UDC678.746.2

Research on Heat-Resistant Styrenic Polymer (MSα)

Masao Kimura*1
Keiichi Saito*1
Ikuro Yamaoka*1
Toshihiro Yamamoto*1
Toshimasa Tanaka*1

Abstract:

To enhance the heat resistance of polystyrene (PS), a commodity plastics, its copolymerization with α-methylstyrene (αMS) was studied, and as a result its service temperature limit could be increased by about 50°C. When αMS is contained in a resin system, it is susceptible to thermal decomposition. In the newly developed polymerization process, depolymerization proceeds along with polymerization at a temperature higher than the ceiling temperature. As a result, chemical bonds that tend to decompose can be avoided to improve the molding stability. Further, a continuous bulk polymerization process that can industrially synthesize an α-methylstyrene-methyl methacrylate copolymer (MSα) was developed by changing catalyst and other polymerization conditions. This new process compensates for the decrease of reaction rate due to depolymerization. The resultant MSα copolymer possesses the highest surface hardness and flexural modulus among thermoplastic resins.

1. Introduction

Commodity resins are confronted with mounting market demands focused on high performance. A group of Nippon Steel Corporation is strongly urged to improve the heat resistance of its polystyrene products[1]. The heat resistance of noncrystalline resins is raised generally by introducing bulky repeating units into their chemical structure and increasing the stiffness of their main chains[2].

Among widely used monomers are maleic anhydride, maleimide, and α-methylstyrene (αMS). αMS is often used in free-radical bulk polymerization to increase the heat resistance of styrenic system resins because it is highly soluble to styrene and requires no specific solvents. However, a reaction system containing αMS is markedly low in reaction rate. Moreover, low-molecular weight by-products are generated to the detriment of properties, especially heat resistance. Other polymerization processes, anionic polymerization, for example incur so high production cost that they are not feasible.

αMS itself has high heat resistance, but is susceptible to thermal decomposition because of the steric hindrance of the main chains that are composed of a bulky methyl group. Poly (α-methylstyrene) homopolymer also has excellent heat resistance with a glassy transition temperature of 185°C, but its ceiling temperature is low at 61°C. It is thermally decomposed when molded, and therefore cannot be used as a molding material[3]. When copolymerized with another monomer, αMS is liable to thermal decomposition if there are arranged three or more repeating units.

*1 Technical Development Bureau

A high-αMS composition therefore cannot yield an appropriate structural material. On the other hand, a low-αMS composition should be capable of providing a molding material less susceptible to thermal decomposition when αMS is copolymerized with another monomer at a temperature above the ceiling temperature. A high-molecular weight polymer is difficult to produce by high-temperature polymerization, but is considered polymerizable by the use of a suitable catalyst.

We investigated the synthesis of a random copolymer (MSα) of αMS and methyl methacrylate (MMA) to produce a styrenic resin with high heat resistance and modulus of elasticity. The chemical structure of MSα is as shown in **Fig. 1**. MSα was developed as a heat-resistant grade of ESTYRENE MS manufactured and marketed by Nippon Steel Chemical Co., Ltd.

MSα itself has already been studied, but has not yet been commercialized because it is extremely difficult to manufacture[4]. In other words, it is low in the polymerization rate and therefore is difficult to post-process. It may be polymerized by emulsion polymerization and solution polymerization. Study was made of the synthesis conditions necessary for the production of an αMS copolymer by the continuous bulk polymerization process that is most cost effective because existing facilities can be diverted. The production process also includes devolatilization to remove unreacted monomers and disposal of additives. These additional steps, however, are not discussed here.

The copolymer thus obtained exhibited excellent heat resistance as expected. Its properties can be improved further by copolymerization with a third monomer such as styrene, acrylonitrile, or maleic anhydride. This report also presents the improvement of fluidity by copolymerization with styrene without sacrificing heat resistance.

2. Experimental

2.1 Methods

Polymerization was performed in a 120-ml autoclave. The extent of conversion was determined by diluting the reaction solution with chloroform, dropping the solution into methanol, and weighing the solid sedimentation after settling. A molecular weight calibration curve was prepared from styrene with standard molecular weight, and the molecular weight of the copolymer was measured by a gel-permeation chromatography (GPC) system made by Tosoh. The monomer composition ratio of the copolymer was determined from the proton ratio of the methoxy group of MMA to the phenyl group of αMS as measured by a ^{1}H-NMR spectrometer (JEOL FX90Q).

The copolymer composition ratio was determined by adjusting the time to obtain a conversion rate of 10% or less at the reaction temperatures of 100, 120 and 140°C in the polymerization experiment in which thermal polymerization was performed using an ampoule containing no initiators. Peroxides were used as initiators to analyze the time-conversion rate relationship and other conditions essential for continuous polymerization. The copolymer was produced by varying the peroxides from monofunctional to tetrafunctional types, by which the conversion rate, molecular weight, composition, and other factors were investigated.

The product copolymer was mixed with an apropriate amount of antioxidant, molded into round dumbbell specimens using a Mini-Max injection molding machine of CSI, and tested according to JIS methods.

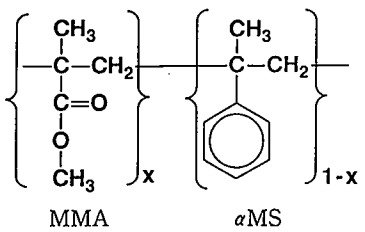


Fig. 1 Chemical structure of MSα

MMA is methyl methacrylate, αMS is α-methylstyrene, and x is molar ratio

2.2 Results

2.2.1 Monomer concentration of copolymer

Fig. 2 shows the reaction temperature dependence of a copolymer composition curve that indicates the relationship between the monomer concentration of the charge stock and the monomer concentration of the product copolymer. The αMS content of the copolymer largely depends on the reaction temperature. Compared with MMA, αMS is incorporated in the polymer increasingly with decreasing temperature, and vice versa. At reaction temperatures of 140°C and above, no copolymers can be formed that contain more than 20 mol% of α-methylstyrene (αMS).

In the case of copolymerization, reactivity varies according to the combination of monomers. For ordinary vinyl copolymerization, the reactivity ratio is generally determined as a reaction rate constant ratio of the growth reaction formulas, as shown in **Fig. 3**. Methods for obtaining the copolymerization reactivity ratios r_1 and r_2 are available in literature and are not discussed in detail here. Three principal methods may be cited here: 1) the intersection method; 2) the Finemann-Ross method; and 3) the Mayo-Lewis integration method[5]. **Table 1** shows the temperature dependence of r_1 and r_2 as obtained by these methods.

The reaction of styrene and αMS at 100°C is investigated by other researchers, and the copolymerization reactivity ratios $r_1 = 0.01$ and $r_2 = 60$ are obtained[2]. When these values are compared with the MMA-αMS copolymerization reactivity ratios $r_1 = 0.0$ and $r_2 = 0.9$ obtained in the present study, it is evident that the α-position methyl of MMA has an influence on the reac-

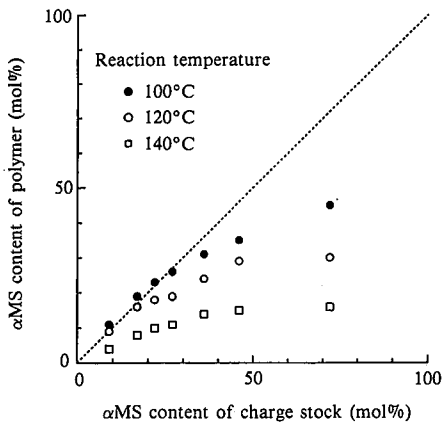


Fig. 2 Temperature dependence of MSα copolymer composition ratio

$$\text{——}M_1* + M_1 \xrightarrow{k_{11}} \text{——}M_1\text{-}M_1*$$
$$\text{——}M_1* + M_2 \xrightarrow{k_{12}} \text{——}M_1\text{-}M_2*$$
$$\text{——}M_2* + M_1 \xrightarrow{k_{21}} \text{——}M_2\text{-}M_1*$$
$$\text{——}M_2* + M_2 \xrightarrow{k_{22}} \text{——}M_2\text{-}M_2*$$

M_1 : αMS, M_2 : MMA
$r_1 = k_{11}/k_{12}$, $r_2 = k_{21}/k_{22}$
*Free radical

Fig. 3 Copolymerization reaction formulas

Table 1 Values of r_1 and r_2 calculated by three methods

Reaction temperature (°C)	100		120		140	
Copolymer reactivity ratio	r_1	r_2	r_1	r_2	r_1	r_2
Intersection method	0	0.9	−0.2	1.2	−0.4	2.8
Finemann-Ross method	0	0.9	−0.1	1.3	−0.3	2.9
Mayo-Lewis method	0	0.9	−0.3	1.2	−0.3	2.8

tion rate as a steric hindrance. Styrene-styrene bonding exerts no or little effect on the reaction involved because the group that produces the steric hindrance is hydrogen, and r_2 assumes a large value.

Generally, r_1 and r_2 are said to be little affected by the reaction temperature[5], but was greatly affected in the reaction discussed here. As evident from **Table 1**, the three methods provide almost the same values of r_1 and r_2. The value of r_1 is zero or negative, which suggests that the copolymerization reaction type is different from the conventional one. As the reaction temperature rises, the value of r_1 decreases, while the value of r_2 increases.

The value r_1 is a reaction rate constant ratio as mentioned above and is $r_1 = k_{11}/k_{12}$, as shown in **Fig. 3**. Since the αMS homopolymer is generally depolymerized at this temperature, k_{11} is considered negative. In other words, an αMS monomer is presumed to be added to the polymer chain which is terminated by the αMS free radical in a manner contrary to the conventional reaction in which an αMS free radical is freshly formed, or the depolymerization is presumed to take place. The reaction formulas therefore should take into account depolymerization, as shown in **Fig. 4**[6]. Since the ceiling temperature of the MMA homopolymer is 164°C, the depolymerization of MMA need not be considered in the reaction temperature range of 100 to 140°C. Verification of this reaction mechanism calls for more precise experiments, and will be described in subsequent reports.

2.2.2 Application to continuous bulk polymerization process

(1) Effect of initiator

Since polymerization is carried out at a high temperature, its reaction competes with the depolymerization reaction and is low. Study was made to improve the molecular weight loss by rendering initiators multifunctional. **Fig. 5** shows the chemical structures of representative initiators among the many initiators with different functional groups studied. **Table 2** gives the molecular weight, conversion, and αMS content of polymers polymerized using these initiators so that the functional group concentration would become constant. It is clear from the table that the molecular weight increases with increasing number of functional groups. Polymers with equal conversion degree and equal composition together with high molecular weight could be successfully produced through the use of multifunctional initiators. In other words, the molecular weight is considered to increase in a way that the polymer grows with polymer chains branching from the multifunctional initiator. No change is presumed to take place in the conversion or composition, because the type of polymerization itself does not change with or without initiators.

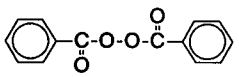
(2) Time dependence of conversion and molecular weight

On the basis of the above results, MSα was polymerized at the monomer charge ratio of 70/30 mol% using Percadox 12 as the initiator, and the time dependence of conversion was investigated. The conversion rate was determined by keeping the initiator concentration constant and changing the reaction temperature. The test results are as shown in **Fig. 6**. As indicated, the conversion rate increases with increasing reaction temperature, but when the reaction temperature exceeds 120°C, it decreases with increasing reaction time. The change of conversion rate with reaction time is steep as the reaction temperature approaches 120°C, but is moderated as the reaction temperature surpasses 120°C.

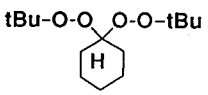
The reason why the conversion rate increases with increasing reaction temperature up to 120°C may be explained as follows. The temperature at which the amount of the initiator used is halved in one and a half hours is 118°C. At lower temperatures,

$$\text{——}M_1* + M_1 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{——}M_1\text{-}M_1*$$
$$\text{——}M_1* + M_2 \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \text{——}M_1\text{-}M_2*$$
$$\text{——}M_2* + M_1 \underset{k_6}{\overset{k_5}{\rightleftharpoons}} \text{——}M_2\text{-}M_1*$$
$$\text{——}M_2* + M_2 \underset{k_8}{\overset{k_7}{\rightleftharpoons}} \text{——}M_2\text{-}M_2*$$

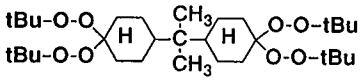
Fig. 4 Copolymerization reaction formulas with depolymerization taken into account



Benzoyl peroxede
Perbutyl A (Kayaku Akzo)



1, 1-Di-t-butyl peroxy cyclohexane
Trigonox 12 (Kayaku Akzo)



2, 2-Bis (4,4'-di-t-butyl peroxy cyclohexyl) propane
Percadox 12 (Kayaku Akzo)

Fig. 5 Chemical structures of initiators

Table 2 Molecular weight, conversion rate, and αMS content of MSα copolymers produced by using different initiators

Initiator	Perbutyl A	Trigonox 12	Percadox 12
Molecular weight (x 10^4)	5.40	7.73	8.64
Conversion rate (%)	47	43	44
αMS content (mol%)	18	18	19

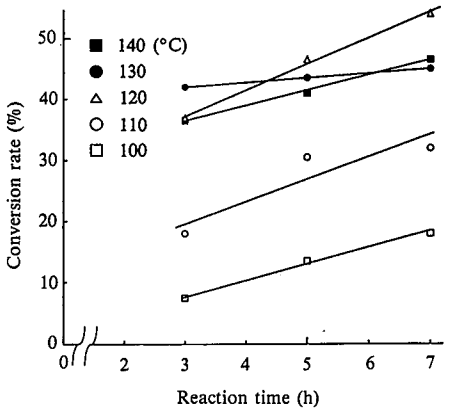


Fig. 6 Reaction temperature dependence of changes with time in conversion rate

the decomposition of the initiator is retarded (the half life of the initiator is 4 h at 100°C and 2 h at 110°C), the generation of free radicals is decreased, and the rate of polymerization is lowered. In addition, since a large amount of initiator still remains, polymerization freshly proceeds to increase the conversion rate. At higher temperatures, the initiator is decomposed too fast (the initiator concentration is halved every 10 min as the reaction temperature rises to 140°C). Further, the reaction solution gains fluidity with the result that the initiator is depleted before the viscosity necessary for the gel effect to promote the polymerization is reached, that is, before a high conversion rate is achieved. The subsequent polymerization proceeds only as thermal polymerization and therefore the conversion rate does not rise any longer.

The αMS content of the polymer is the same as shown in **Fig. 2**, and it decreases with increasing reaction temperature. It is thus confirmed that polymerization proceeds in the same manner, irrespective of whether or not initiators are used, and that the monomer composition in the reaction solution changes but not to the extent of bringing about any significant effect on the polymer composition.

The above results indicate that polymerization can be effected most efficiently at 120°C when an initiator is used.

(3) Initiator concentration dependence of conversion rate and molecular weight

To determine the optimum initiator concentration for use, study was made on the effects of initiator concentration at 120°C on the conversion rate and molecular weight. The results are as shown in **Figs. 7** and **8** respectively for the conversion rate and molecular weight. When no initiator is used, only thermal polymerization occurs so that the conversion rate is low and the molecular weight is high. The conversion rate increases with increasing initiator concentration, but as the molecular weight decreases as shown in **Fig. 8**, the reaction time must be extended. The higher the conversion rate, the higher the reaction efficiency. As the conversion rate increases, the MSα reaction solution becomes too high in viscosity, so that devolatilization and subsequent steps are hindered. In designing a commercial production process, therefore, the initiator concentration and reaction time must be optimized to suit the desired molecular weight.

2.2.3 Properties of MSα

Fig. 9 shows the effect of the αMS content on the glassy transition temperature (T_g). The glassy transition temperature of random copolymers generally follows Fox's equation[7].

$$\frac{1}{T_g} = \frac{W_1}{T_{g_1}} + \frac{W_2}{T_{g_2}}$$

where W_1 is the molar ratio of the αMS monomer; W_2 is the molar ratio of the MMA monomer; T_{g_1} is the glassy transition temperature of the αMS homopolymer; and T_{g_2} is the glassy transition temperature of the MMA homopolymer. The dotted line in **Fig. 9** indicates the glassy transition temperature predicted by Fox's equation, connecting the glassy transition temperatures of the poly(α-methylstyrene) [P(αMS)] and poly(methyl methacrylate) (PMMA) homopolymers. The glassy transition temperature of the system of interest is higher than the predicted glassy transition temperature. This means that the steric hindrance due to the phenyl group at the α position is very effective in improving heat

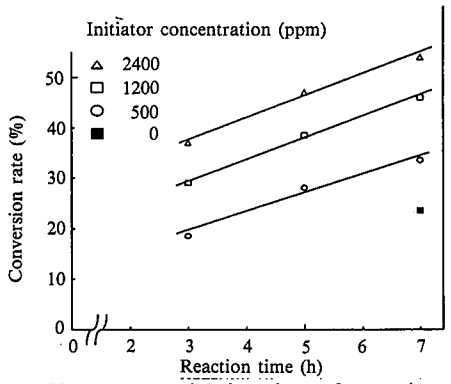


Fig. 7 Initiator concentration dependence of conversion rate

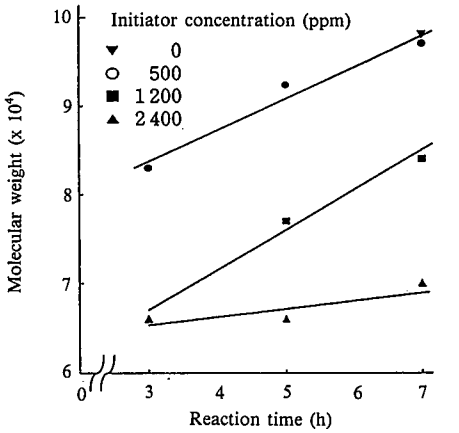


Fig. 8 Initiator concentration dependence of molecular weight

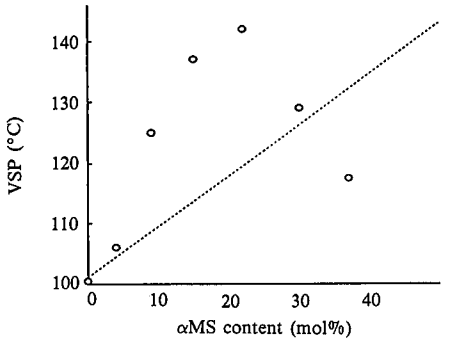


Fig. 9 αMS content dependence of Vicat softening point (VSP)

resistance. The predicted and measured glassy transition temperatures practically agree for the above-mentioned styrene copolymer system, indicating that the improvement in heat resistance varies with the magnitude of steric hindrance.

The glassy transition temperature T_g steeply increases as the αMS content of the main chain increases to 25 mol%, but decreases as it exceeds 25 mol%. This is probably because the thermal decomposition of αMS produces low-molecular weight substances, which play a plasticizer-like role in lowering the glassy transition temperature. This thermal decomposition itself can be improved to some extent by mixing an antioxidant.

Table 3 summarizes the mechanical and thermal properties of MSα with 20 mol% αMS and 20 mol% MSα-S modified by styrene (S) as described in the next section. The properties of PMMA are also given for comparison. Each resin is very clearly transparent. The major shortcomings PMMA, that is, heat resistance (glassy transition temperature and Vicat softening point) and water absorption, are improved by copolymerization with αMS. The heat resistance of MSα, in particular, is comparable to those of engineering plastics. Reflecting the stiffness of the main chain, αMS possesses a flexural modulus which is superior to that of PMMA, and has a value closest to the highest among thermoplastic resins. The tensile strength and tensile impact value of MSα are also better than those of PMMA. The surface hardness is higher than originally expected. PMMA is most resistant to scratching except for crosslinked thermosetting resins and is used in aircraft windows. MSα has the highest pencil hardness among thermoplastic resins.

2.2.4 Modification of MSα

MSα is reduced in fluidity for the improvement of heat resistance and is therfore more difficult to mold than general styrenic resins. An attempt was made to improve its fluidity without hampering its heat resistance by copolymerizing with styrene. Experiments made under the usual reaction conditions showed that αMS can be copolymerized with styrene in the very same manner as MSα.

MSα was then copolymerized with styrene by changing the monomer charge ratio and keeping the αMS content constant at 23 mol%. **Fig. 10** shows the styrene content dependence of the melt index (MI), a measure of fluidity, and the glassy transition temperature (T_g) of the terpolymer obtained. As the styrene content increases up to 20 mol%, T_g drops slightly, while MI rises. This means that the 20 mol% MSα terpolymer has its fluidity improved while retaining its high heat resistance. As the styrene content increases further to 25 mol%, however, MI increases but T_g drops by as much as 20°C. Other properties become closer to those of PMMA by the degree of MMA replacement with styrene, except for the water absorption rate which can be reduced to alleviate the deterioration of mechanical and thermal properties in service, and to improve treatments preliminary to molding.

Table 3 Main properties of MSα, MSα-S, and PMMA

Property	MSα	MSα-S	PMMA
Glassy transition temperature (°C)	149	136	102
Vicat softening point (°C)	140	130	98
Tensile strength (MPa)	85	74	66
Flexural modulus (GPa)	3.3	3.2	2.7
Tensile impact value (J)	3.2	1.3	1.3
Rockwell hardness (L scale)	108	103	97
Pencil hardness	4H	3H	2H
Water absorption (%)	0.35	0.31	0.39

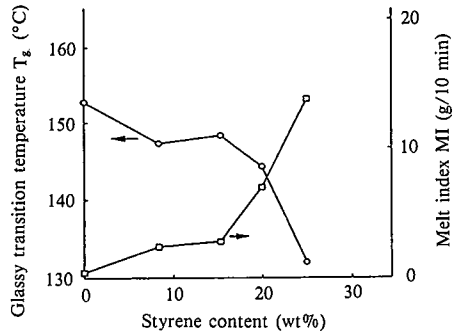


Fig. 10 Styrene content dependence of glassy transition temperature (T_g) and melt index (MI) of terpolymer

3. Conclusions

Descriptions have been focused on the results of researches made of the copolymer composition and reaction type of MSα as well as its commercial polymerization conditions. This reaction system is a special case in which polymerization and depolymerization proceed at the same time. It was found that an αMS system copolymer without bonding with another αMS monomer can be synthesized by optimizing the reaction conditions. This is extremely convenient for the αMS copolymer whose major shortcoming is susceptibility to thermal decomposition, and which is considered responsible for the thermal stability of MSα and its terpolymer compared with the homopolymer.

The MSα copolymer obtained was found to possess excellent heat resistance as expected and the highest flexural modulus among thermoplastic resins. It also features the highest scratch resistance among thermoplastic resins and is expected to find use as a pure material and also as a protective film for clear moldings.

MSα can be modified with extreme ease by other monomers as described for its modification by styrene. Therefore, its compatibility with other resins can be controlled, and it can be utilized as a polymer alloy component. An MSα-polycarbonate polymer alloy, for example, becomes semicompatible, and therefore possesses excellent mechanical properties while retaining pearl luster[8]. It has already been found that a modified MSα can be improved in moldability by reactive processing with crystalline resins. It is expected to find widespread use also in other applications[9].

The study of production process may be branched into the polymerization step, unreacted monomer removal step, and additive disposal and other steps. Among them, only the polymerization step has been dealt with here. The other process steps will be serially discussed in subsequent reports.

References

1) Maul, J., Meyer, H.H.: Makromol. Chem. Macromol. Symp. 53, 23 (1992)
2) Priddy, D.B., Traugott, T.D., Seiss, R.H.: J. Appl. Polym. Sci. 41, 383 (1990)
3) Alfrey, Jr.T., Bohrer, J., Mark, H.: Copolymerization, High Polymer Series. Vol. VIII. Interscience, New York, 1952
4) Vandegaer, J.E.: US Patent 3,135,723. 1964
5) Ham, G.E.: Copolymerization, High Polymer Series. Vol. XVIII. Interscience, New York, 1964
6) Izu, M. et al.: J. Polymer Sci. A-1. 8, 1687 (1970)
7) Fox, T.G.: Bull. Am. Phys. Soc. 1, 123 (1956)
8) Yamamoto, T., Saito, K., Kimura, M.: Polymer Applications. 40, 87 (1991)
9) Saito, K. et al.: Polymer Preprint. 41, 3882 (1992)