Heat Resistant Styrene/α-Methylstyrene Copolymers Made via Continuous Anionic Polymerization at High Temperature

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Synopsis

Styrene/α-methylstyrene (SAMS) copolymers were produced containing up to 67 weight % AMS. The polymerizations were carried out using anionic polymerization at high temperature (100°C) in a CSTR type reactor. The reactivity ratios for the anionic copolymerization of styrene (M_1) and AMS (M_2) were estimated to be $r_1 = 60$ and $r_2 = 0.01$. Thermal degradation of a SAMS copolymer containing 50 weight % AMS was studied and compared with free radical polystyrene (FRPS) and anionic polystyrene (APS). The relative rate of styrene monomer generation for the three polymers followed the order SAMS > FRPS > APS. The relative rate of loss of molecular weight for the three polymers was FRPS > APS > SAMS. This indicates that the main mechanism of thermal degradation of SAMS copolymers is depolymerization rather than chain scission.

INTRODUCTION

Many applications for styrenic polymers require increased heat resistance temperature. One of the most common ways to increase the heat distortion temperature of styrenic polymers is by the addition of a comonomer to increase backbone stiffness. The most common comonomers used to accomplish this are maleic anhydride,[1] maleimides,[2] and α-methylstyrene (AMS). Generally, AMS is the more commonly preferred high heat comonomer since its solubility characteristics are like styrene, thus special polymerization solvents are not needed. However, addition of AMS to the free-radical styrene mass polymerization significantly slows the polymerization rate and increases the amount of oligomer formation. These oligomers reduce the glass transition temperature and cause mold sweat and die drip problems during molding and extrusion.

Recently, it has been reported that the anionic polymerization of styrene is industrially feasible.[3-7] A process to produce broad molecular weight distribution polystyrene ($M_w/M_n = > 2.0$) having excellent color utilizing a continuous stirred tank reactor (CSTR) design was described. Several process and product advantages were found for anionic polymerization of styrene at high temperatures (90–110°C) in a CSTR type polymerization reactor when compared to free-radical polymerization of styrene. Anionic polystyrene was found to be more pure than free-radical polystyrene from the standpoint of contamination by monomer and oligomers, and was also more thermally stable due to the lack of "weak links."[8]

Anionic polymerization is widely used to manufacture block copolymer elastomers containing polystyrene segments. Recently, elastomers containing blocks of styrene/α-methyl-styrene (SAMS) have been described.[9]

In this article we describe the preparation and the properties of SAMS copolymers made using anionic polymerization at 100°C in a CSTR type reactor.

EXPERIMENTAL

Polymerization

The basic process used for this study was as previously described.[4,11] High purity (> 99.8%) styrene (stabilized with 3 ppm 4-t-butylcatechol) and ethylbenzene (EB), that had been freshly distilled, were used. The AMS used in this study was purchased from USS Chemicals and was manufactured by the dehydrogenation of cumene. AMS made by the oxidation-dehydration of cumene was found to contain high levels of acetophenone which interfere with anionic polymerization.

The ratio of unreacted monomers in the polymerization reactor at steady state was measured as follows: a sample of polymer syrup (1 part) was shaken for 1 h in hexane (100 parts) containing 1% by weight acetic acid. The liquid phase was analyzed using a gas chromatography to determine the ratio of AMS to styrene.

Polymer Degradation

Sample preparation: Each polymer (20 g) was dissolved in 500 mL of reagent grade toluene. The solution was added slowly to 1500 mL of rapidly stirred HPLC grade methanol. The precipitated polymer was removed by filtration and reprecipitated using the same procedure. The twice precipitated polymer was dried at 215°C and 10 mmHg for 15 min. The resin was then pulverized using a mortar and pestle.

Degradation Procedure

The purified resin powder (1 g) was sealed in a glass ampoule under 1 mmHg. The ampoule was placed in a Wood's metal bath at 250, 275, or 295°C. Analysis of the degraded polymer samples for styrene and AMS formed during the thermolysis was performed using gas chromatography.

Molecular Weight Analysis

The degraded polymer samples were dissolved in tetrahydrofuran to 0.25 weight % polymer. The molecular weight of the samples was determined using size exclusion chromatography (SEC). Two 8 mm × 30 cm, 10 μm particle size mixed bed SEC columns manufactured by Polymer Laboratories were used in series. The eluent was THF which was pumped at 1 mL/min. Column linearity was confirmed using monodisperse polystyrene standards. The columns were calibrated against a broad dispersity polystyrene (M_w = 250,000 and M_n = 100,000). The M_w of the SAMS copolymer (48 mole % AMS) used for the thermal degradation study was analyzed to be 200,000 by the SEC method and 216,000 using low angle lazer light scattering (LALLS).[10] It is assumed that the 8% discrepancy between SEC and LALLS M_w data remained constant during the degradation study.

Thermal Analysis

A DuPont 1090 Thermal Analyzer was used to determine the glass transition and decomposition of SAMS copolymers. The heating rate was 20° C/min.

RESULTS

The ceiling temperature for AMS is 61°C;[9] therefore to make AMS homopolymer the polymerization must be carried out below this temperature. The homopolymer of AMS has very poor thermal stability, unzipping to monomer upon heating.[11] Copolymerization of AMS with styrene will not yield AMS sequences of longer than diad if the polymerization is carried out at temperatures above the ceiling temperature.[9]

Figure 1 compares monomer ratio versus copolymer composition data for anionic polymerization in batch[12] and CSTR processes (SAMS copolymer compositions were determined using ^{13}C NMR).

When n-butyllithium is added to a mixture of styrene and AMS in a batch mode at temperatures > 61°C, the styrene quickly polymerizes leaving most of the AMS behind due to the low reactivity of AMS. Thus, to produce a SAMS copolymer containing significant levels of AMS requires a high monomer ratio of AMS to styrene. For example, to make a SAMS copolymer containing 45% by weight AMS would require that the starting monomer mixture consist of 95% by weight AMS and 5% styrene. When the styrene is consumed, the polymerization stops. The final solution after polymerization consists of 10% by weight SAMS and 90% by weight unreacted AMS monomer. Isolation of the SAMS from this mixture is difficult due to its low concentration and the relatively low vapor pressure of AMS monomer.

Anionic copolymerization of styrene and AMS in a CSTR at > 61°C allows the manufacture of polydisperse and homogeneous high AMS containing SAMS in concentrated (50% by weight polymer) solution containing up to 66.7 mole % AMS (69.04% by weight).
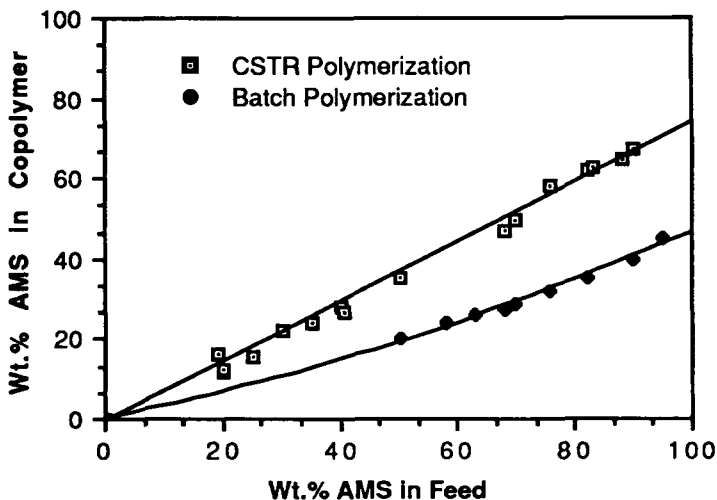

Fig. 1.   Anionic copolymerization of AMS and styrene at 100°C.

During anionic copolymerization of styrene at steady state in a highly mixed CSTR, the styrene concentration is very low because it immediately reacts. However, AMS is always in high concentration because of its low reactivity. The living SAMS polymer chains are in a constant environment consisting of low styrene and high AMS concentrations (Table I). The result is the formation of SAMS containing a high amount of AMS incorporation.

Figure 1 clearly shows the advantage of the CSTR configuration for making high AMS containing SAMS. This data gives experimental confirmation of the theoretical maximum[9] of about 69% by weight AMS in the copolymer. The polydispersity of the SAMS made using batch polymerization ranged from 1.1 to 1.5. The polydispersities of the CSTR prepared SAMS were all about 2.0.

With the data from Figure 1, the reactivity ratios can be calculated using eq. (1) if the unreacted monomer ratios at steady state in the CSTR are known (assuming that the polymer is in equilibrium with the monomers).

$$\frac{m_1}{m_2} = \frac{1 + r_1 \dfrac{M_1}{M_2}}{1 + r_2 \dfrac{M_2}{M_1}} \tag{1}$$

where m_1 and m_2 are the mole fraction of monomer 1 and 2 in the polymer and M_1 and M_2 are the mole fraction of unreacted monomers 1 and 2 at steady state in the CSTR.

The polymer compositions and ratios of the unreacted monomers in the reactor at steady state were measured during the production of two SAMS copolymers. The results are shown in Table I.

Iterative trial and error calculations using this data set show the r_1 and r_2 are 60 and 0.01, respectively (since only a minimum data set was used, this is only an approximation).

Incorporation of AMS into polystyrene using anionic chemistry is very effective in raising the glass transition temperature (T_g) (Fig. 2).

The T_g data follows the Fox equation (eq. (1)).[13]

$$\frac{1}{T_g} = \frac{W_1}{T_{g_1}} + \frac{W_2}{T_{g_2}} \tag{2}$$

where W_1 and W_2 are the weight fraction of the two monomers in the polymer.

THERMAL DECOMPOSITION

The rate of monomer generation and molecular weight degradation of a SAMS copolymer containing 48 mole % AMS was determined by *in vacuo*

TABLE I
Ratio of Monomers in the CSTR and Polymer at Steady State

Experiment number	m_1/m_2[a]	M_1/M_2[a]
1	3.49	0.0516
2	1.24	0.0167

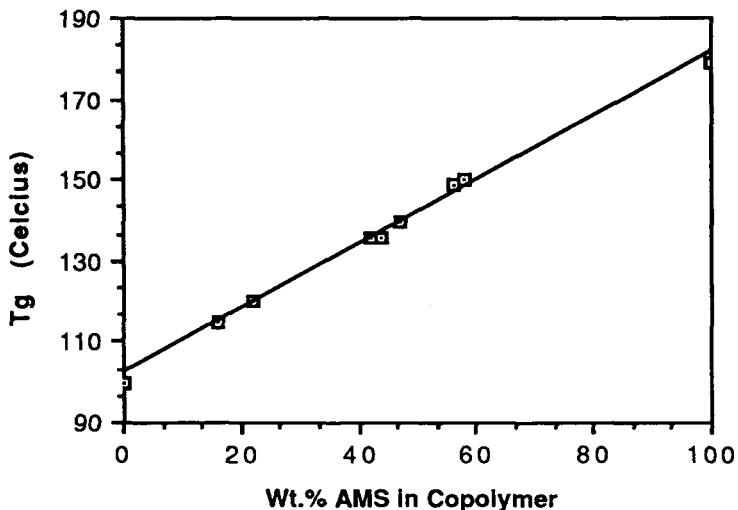[a] Suffixes 1 and 2 are styrene and AMS, respectively.

Fig. 2.   The glass transition temperature of SAMS copolymers made using anionic polymerization.

thermolysis at 250, 275, and 295°C. A commercial free radical polystyrene and an anionic polystyrene (prepared during a previous study)[5] were thermolyzed under the same conditions for comparison of degradation rates. Figures 3 and 4 show the rates of monomer generation (ppm/h) and loss of weight average molecular weight (calculated in atomic mass unit/h) respectively.

This data was used to derive the Arrhenius rate equations (assuming an apparent zero order dependence on the polymer concentration) for styrene monomer generation and molecular weight loss of the form
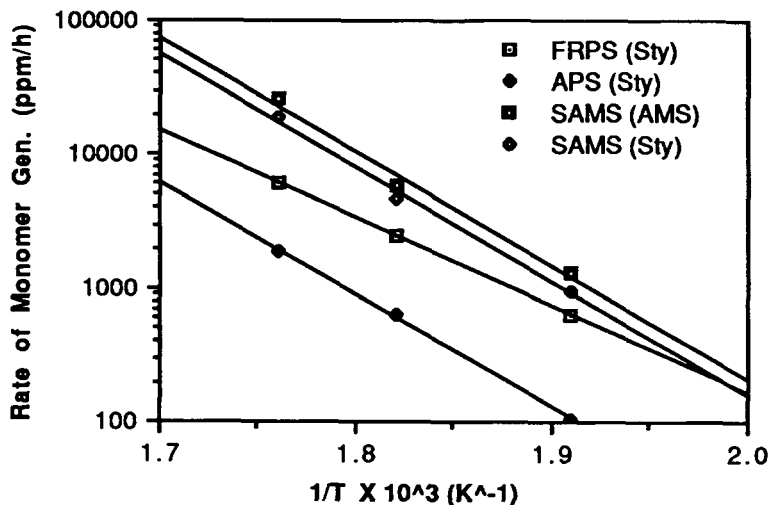
$$k = Ae^{-E/RT}$$

Fig. 3.   Rate of monomer generation upon thermolysis.

where:

k = rate of volatile formation in ppm/h or molecular weight loss in amu/h
A = frequency factor
E = activation energy in cal./mole
R = gas constant in cal. mole^{-1} K^{-1} = 1.986
T = temperature in K

Styrene Generation

FRPS

$$k = 3.0576 \times 10^{13} e^{-29834/RT}$$

APS

$$k = 4.17559 \times 10^{15} e^{-37926/RT}$$

SAMS

$$k = 5.37485 \times 10^{17} e^{-38731/RT}$$

M_w Degradation

FRPS

$$k = -2.70506 \times 10^{6} e^{-16828/RT}$$

APS

$$k = -2.93180 \times 10^{8} e^{-22730/RT}$$

SAMS

$$k = -1.43027 \times 10^{13} e^{-35330/RT}$$

SAMS shows a fast rate of monomer generation which is accompanied by a slow loss of molecular weight. This indicates that SAMS copolymers thermally degrade mainly by undergoing depolymerization rather than main chain breakage relative to polystyrene. This phenomenon has also been reported for the AMS homopolymer.[11]

The increased heat resistance of SAMS results in an increase in melt viscosity. In order to fill the mold during injection molding, the fabrication temperature has to be increased as the AMS content increases. Figure 5 shows the molding temperature required for SAMS copolymers to fill a mold, under typical molding pressures, as compared to the temperature at which incipient weight loss occurs during thermal gravimetric analysis (20°C/min heating rate under nitrogen). The thermal stability of SAMS decreases as the AMS content increases but copolymers up to 69% by weight AMS are easily fabricated without decomposition.
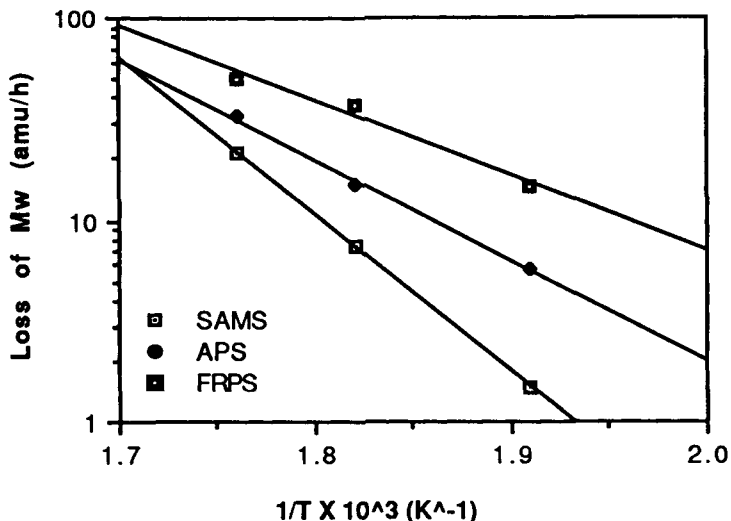
Fig. 4.   Rate of M_w loss upon anaerobic thermolysis.

When adding a comonomer to styrenic polymers to increase heat resistance, the tensile strength properties generally increase. This trend is also observed for SAMS copolymers. Figure 6 shows the increase of the tensile strength of various SAMS copolymers all having a weight average molecular weight (M_w) of about 200,000 (using size exclusion chromatography (SEC) calibrated against polystyrene standards).

CONCLUSIONS

Utilizing anionic polymerization at high temperature in a CSTR type reactor, random SAMS copolymers can be produced containing up to 67 mol % (69
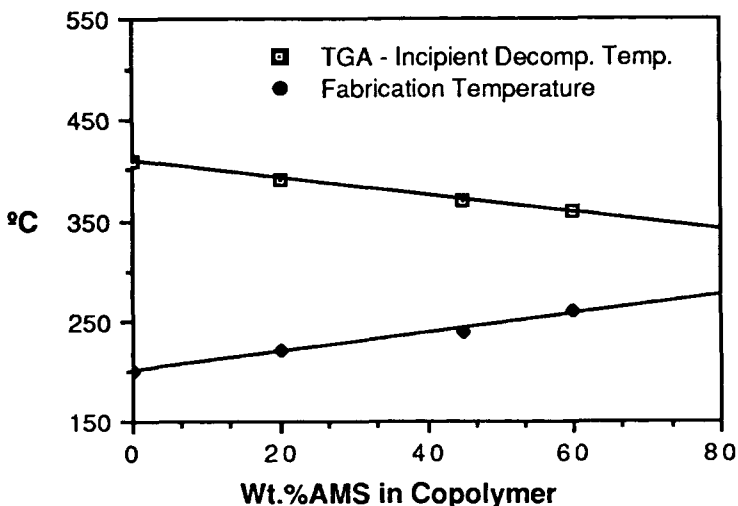
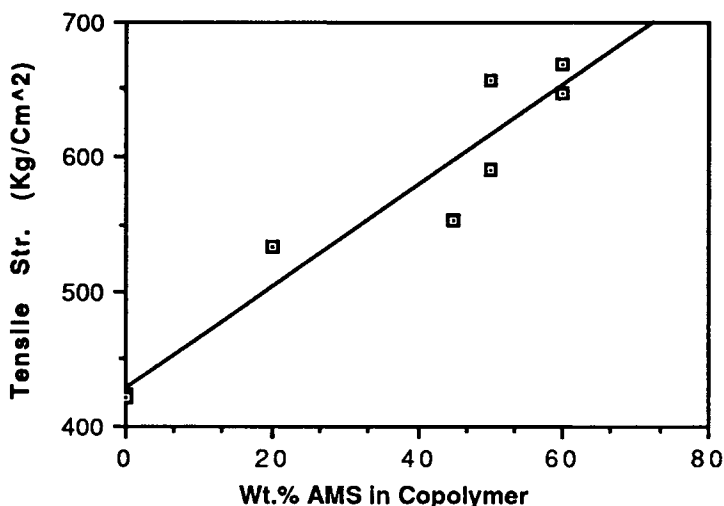Fig. 5.   SAMS composition versus stability/fabrication.

Fig. 6.   Tensile strength of SAMS copolymers.

weight %) AMS. These copolymers show improved tensile strength and heat distortion properties over polystyrene. Anionic SAMS copolymers offer good retention of molecular weight upon prolonged heating but quickly form monomer indicating that depolymerization is the main mechanism of thermal degradation.

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