

Structural Modification of Expandable Polystyrene. I. Copolymerization with α -Methylstyrene

Isa Taşkıran,^{1,3} Gürkan Sunal,² Erol Erbay,¹ Nurseli Uyanik²

¹R&D Center, Petkim Petrochemical Holding, Incorporated, 41470 Körfez, Kocaeli, Turkey

²Department of Chemistry, Istanbul Technical University, 80626 Maslak, Istanbul, Turkey

³Civil Aviation College, Kocaeli University, 41285 Arslanbey, Kocaeli, Turkey

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ABSTRACT: Conventional expandable polystyrene (EPS) was modified by the preparation of copolymers containing 1.0, 2.5, and 5.0% α -methylstyrene. Increasing the glass-transition temperature of EPS was the aim of this work. Copolymeric expandable polystyrene (CEPS) samples were characterized with various techniques. ¹H-NMR spectroscopy was used for the determination of the composition, and gel permeation chromatography was used for the determination of the molecular weights and molecular weight distributions. Differential scanning calorimetry showed that the

glass-transition temperatures of the CEPS samples increased with increasing α -methylstyrene contents. The prevention of the collapse of the EPS cells was observed in scanning electron microscopy images of the inner portions and outer surfaces of the CEPS samples. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 609–614, 2003

Key words: polystyrene; modification; synthesis; structure–property relations

INTRODUCTION

Expandable polystyrene (EPS) can be achieved by a suspension polymerization process. Suspension polymerization is the most important polymerization process for styrene homopolymerizations and copolymerizations.¹ In this process, the water/styrene phase ratio is selected to be 1/1 or 3/1 for the production of polystyrene.^{2,3} The monomer is suspended as droplets in the water phase with the aid of mixing, and it is stabilized by a suspending agent. The stabilization of the monomer droplets in the aqueous phase is a basic problem in suspension polymerization.^{4,5} The mechanisms of suspension stabilization are complex.⁶ Various organic and inorganic stabilizers can be used. Organic suspension stabilizers are generally poly(vinyl alcohol) (PVA), poly(vinyl pyrrolidone), and methyl cellulose. Inorganic suspension stabilizers are basically calcium phosphate and magnesium phosphate.^{7–10}

Suspension polymerization occurs in the presence of suspension stabilizers and styrene-soluble polymerization initiators. The monomer droplets, in the presence of suspension stabilizers, are prevented from clumping or agglomerating by agitation during polymerization, especially in higher exothermic cycles. Each monomer droplet in a suspension medium is

considered to be a small bulk polymerization reactor. The kinetics of polymerization within each droplet are the same as those for the corresponding bulk polymerization.¹¹ The blowing agent is introduced into the closed suspension reaction vessel during the final stage of polymerization.¹² After the final polymerization, pentane is impregnated into the polystyrene beads while they are still suspended. The impregnated beads are then centrifuged and dried.

The bead size and distribution, among the most important parameters in suspension polymerization, can be controlled by special techniques.^{13–15} The bead size and distribution are extremely dependent on the reactor geometry and agitation. In this field, the fundamental effect of agitation has been studied by several investigators.^{16–21} The suspending agent can also affect the particle size and distribution of the product.^{22–24}

Conventional EPS also contains a physical blowing agent, such as pentane, pentane isomers, butane, or water.^{25–28} This blowing agent is capable of expanding the compact polystyrene beads upon the heating of the material above its glass-transition temperature (T_g). The vapor pressure of the blowing agent forces the softened polystyrene matrix to expand, and a homogeneous cellular structure with irregular and polyhedral closed cells is formed.²⁹ Beads can be expanded in a pre-expansion operation to preform the beads and remove most of the expansion agent. After this, the beads can be molded to produce several consumer products, including hot drink cups, ice chests, and foam packaging. The expandable beads can also be

Correspondence to: I. Taşkıran (isataskiran@hotmail.com).

TABLE I
Synthesis Condition of EPS

Sample	Amount of monomer (phm)	
	Styrene	α -Methylstyrene
EPS.01	100.0	0.0
EPS.02	99.0	1.0
EPS.03	97.5	2.5
EPS.04	95.0	5.0

molded into very large blocks that can then be cut into sheets for thermal insulation.³⁰

This article reports polystyrene being modified with α -methylstyrene to enhance T_g of the polymer for use in applications such as hot drink cups and food containers. The effects on the chemical structure, molecular weight, and molecular weight distribution were also examined.

EXPERIMENTAL

Materials

Polymerization-grade (99.9%) styrene monomer was provided by Petkim Petrochemical Co. (Kocaelin, Turkey) and used with the inhibitor *tert*-butylcatechol (10 ppm). α -Methylstyrene (99%) was supplied by Merck (Darmstadt, Germany), PVA was purchased from Kuraray (Osaka, Japan), tricalcium phosphate and calcium stearate were obtained from Chemische Fabrik Budenheim (Mainz, Germany), calcium chloride (77%) was supplied by Kemira Kemi (Helsingborg, Sweden), *n*-pentane was purchased from Riedel de Haën A.G. (Seelze, Germany), and linear alkyl benzene sodium sulfonate (LABSS) was supplied by Türk Henkel (Kocaelin, Turkey). The initiator dibenzoyl peroxide (DBPO; 75%) was obtained from Peroxide Chemie GmbH (Munich, Germany), and the initiators tertiary butyl perbenzoate (TBP) and dicumyl peroxide were supplied by Interchim (Worgl, Austria).

Analyses and tests

The syntheses were carried out in a Buchi Glassuster 5-L metal reaction vessel equipped with an adjustable mechanical stirrer, a thermostat (Haake N3), a temper-

ature indicator and controller, vacuum and nitrogen lines, and a pentane inlet line. The gas chromatography (GC) measurements were performed on a Chrompack CP 901 model machine with a setup consisting of CD-WAX packed columns and a column flow of 2 mL/min. The analyses were carried out between 50 and 210°C. A Normandie Labo Cannon-Fenske SR.200 (E 346) viscometer was used to measure the viscosities of the samples. ¹H-NMR spectra of all the samples were obtained on a Bruker AC (200 MHz). Gel permeation chromatography (GPC) measurements were performed with a setup consisting of a Waters pump (model 600E) and three Ultrastaygel columns with porosities of 10⁴, 500, and 100 Å, respectively. The detection was achieved with a Waters differential refractometer (model 410). All of the samples were characterized by GPC analyses. Tetrahydrofuran was used as the eluent at a flow rate of 1 mL/min. The molecular weights were calculated with polystyrene standards. The thermal characteristics of the samples were measured with a Shimadzu TA-501 DSC-5 model machine. Scanning electron microscopy (SEM) micrographs were taken on a JEOL JXA-840 model electron microscope. The samples were prepared by the precise cutting of the beads and the subsequent application of a gold coating of approximately 200 Å.

Syntheses of EPS and copolymeric expandable polystyrene (CEPS)

Synthesis of EPS

Suspension polymerizations were carried out in a temperature- and stirring-controlled metal reactor. The polymerizations were accomplished in three cycles. In the first cycle, named the mass cycle, styrene monomer was mixed with a small amount of water and suspending agents (TCP). Additives (calcium chloride and LABSS) and initiators (DBPO and TBP) were loaded into the reactor, and the reaction mixture was heated. The amounts of TCP and the initiators were the same for all polymerizations. After the reaction temperature reached 90°C, the reaction was carried out for 2.5 h. An additional suspension, prepared in a separate vessel, was added to the reactor at the end of the mass cycle, and then the low-temperature cycle

TABLE II
Experimental Results After *n*-Pentane Impregnation Stage

Sample	Conversion (%)	Residual monomer content (%)	After pentane impregnation			After expansion
			D_{50} (μ m)	D_{84}/D_{50} (μ m)	Pentane (%)	Density (g/cm^3)
EPS.01	99.41	0.59	960	2.06	5.92	10.98
EPS.02	99.52	0.48	850	1.69	5.99	10.24
EPS.03	99.33	0.67	740	1.65	5.58	12.58
EPS.04	99.25	0.75	770	1.53	5.35	17.17

TABLE III
Characterization of EPS Sample

Sample	M_n	M_w	Polydispersity (M_w/M_n)	Kinematic viscosity (cSt)	T_g (°C)
EPS.01	91,000	152,000	1.67	8.65	110.5
EPS.02	93,000	148,000	1.59	8.01	110.8
EPS.03	98,000	152,000	1.55	8.38	112.5
EPS.04	95,000	164,000	1.73	9.44	112.6

M_n = number-average molecular weight; M_w = weight-average molecular weight.

was started. During the low-temperature cycle, the conversion increased with increasing viscosity, and the monomer slowly became sticky. By the end of this cycle, the conversion reached around 98%. At the end of the low-temperature cycle, the exotherm reached a

maximum, and then PVA, LABSS, and calcium hydroxide were added to the reactor to increase the stability of the suspension medium. The polymerization temperature was increased to 120°C. During the high-temperature cycle (third cycle), the reaction was

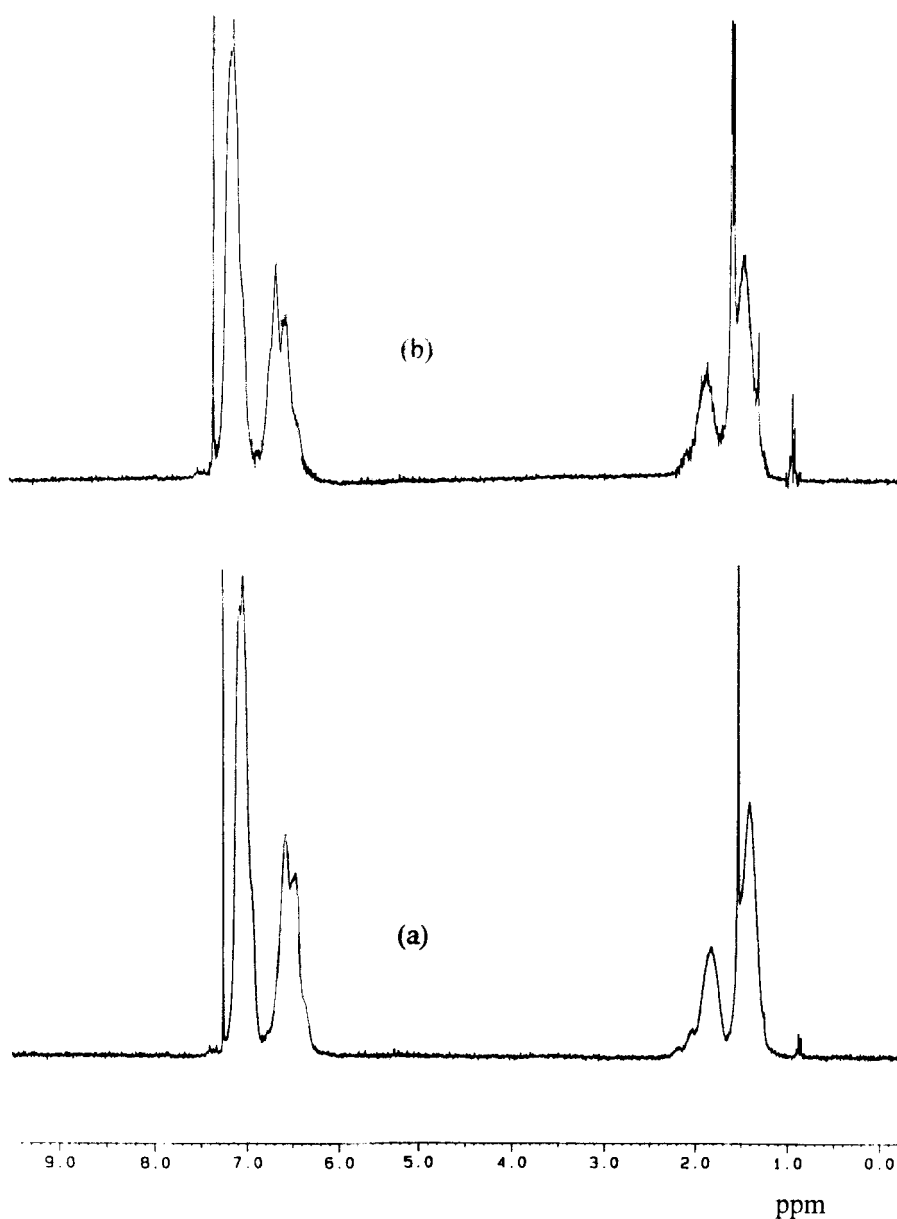


Figure 1 $^1\text{H-NMR}$ spectra of (a) sample EPS.01 and (b) sample EPS.04.

maintained for 2 h to complete the conversion. Then, the reactor content was cooled to 65°C and was purged with nitrogen. *n*-Pentane was added to the reactor for impregnation, and the temperature was again increased to 120°C. The period of the impregnation stage was about 2 h. After this stage, the reactor contents were cooled below 40°C. The phosphate based inorganic suspension stabilizer around the beads was dissolved and removed by the addition of diluted HCl. The obtained polymer slurry was centrifuged first and then dried with a fluidized bed drier below 50°C. After being dried, the beads were screened for the determination of the average particle size and particle size distribution.

Synthesis of CEPS

The same experimental procedure was applied to the copolymerization of styrene with α -methylstyrene. α -Methylstyrene was fed into the reactor at the beginning of the polymerization along with styrene monomer. The synthesis conditions of the styrene homopolymerization and α -methylstyrene/styrene copolymerization are given in Table I.

Characterization

The residual monomer contents after low-temperature and high-temperature cycles were determined by GC analyses. GC was also used to determine the pentane contents of the samples after the pentane impregnation and expansion of the samples. The solution viscosities of the polymers were determined according to the ASTM D 445 standard. Solutions (8%) of the expandable polymer beads in toluene were prepared. The viscosities of the samples were estimated in cst units with a Cannon-Fenske viscometer.

After the expansion of the beads, all the samples were characterized by FTIR qualitatively. The film samples (20 μm) were prepared by the molding method. $^1\text{H-NMR}$ analyses were performed for standard EPS and an α -methylstyrene/styrene copolymeric sample. GPC analyses were performed on the samples for the determination of their molecular weights. The T_g values were determined from the second derivation of the differential scanning calorimetry (DSC) curves in the related temperature zones in the thermograms so that a precise estimation could be made for the observation of very small changes in the T_g values. The heating rate was 10°C/min in all the experiments. SEM micrographs of the samples were taken on the cross sections of the samples (both inner and outer surfaces).

RESULTS AND DISCUSSION

In the preparation of the styrene/ α -methylstyrene copolymer (CEPS), the residual styrene contents were

increased at the end of the low-temperature cycle in comparison with the styrene homopolymerization (EPS). As shown in Table II, the residual monomer content increased if the used amount of α -methylstyrene increased. α -Methylstyrene addition caused retardation in the reaction rate because of steric hindrance.

The molecular weights of the samples were measured by GPC. There were no distinguishable differences between the molecular weights and the distributions, but sample 04 had the highest molecular weight and heterogeneity index because it had the highest (5.0%) α -methylstyrene content. The kinematic viscosities given in Table III also show similar results parallel to the GPC results.

EPS and expandable poly(α -methylstyrene-*co*-styrene) samples were prepared in adequate yields. Standard and modified EPS samples were characterized by $^1\text{H-NMR}$ spectroscopy. $^1\text{H-NMR}$ spectra of sample EPS.01 and EPS.04 are presented in Figure 1(a,b), respectively. As shown in Figure 1(a,b), there were two main peaks: at 6.25–6.83 ppm for protons closer to the main chain of polystyrene and at 6.83–7.20 ppm for protons farther from the main chain of polystyrene. These were the characteristic peaks of polystyrene. Sample EPS.01 [Fig. 1(a)] showed a peak at 1.25 ppm due to the CH_3 group in the polymer. Because there was no proton splitting in this single peak, there had to be a neighboring proton in the CH_3 group. This indicated that homo-polystyrene contained styrene homologue impurities such as α -methylstyrene. The

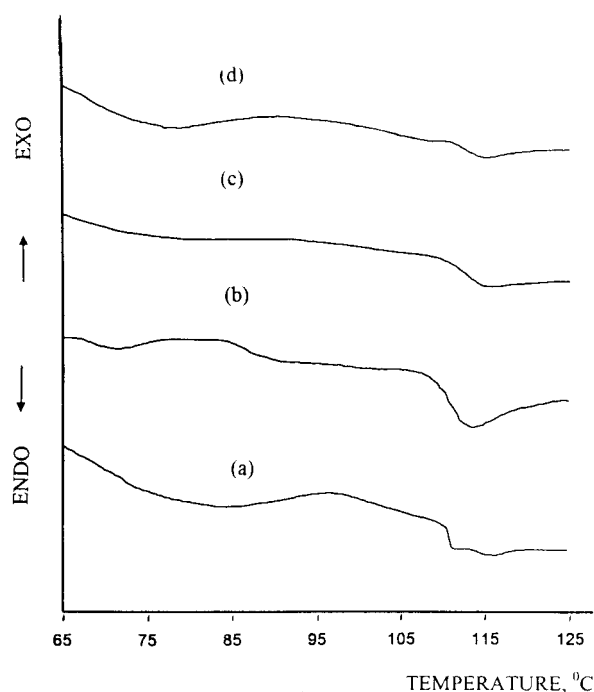
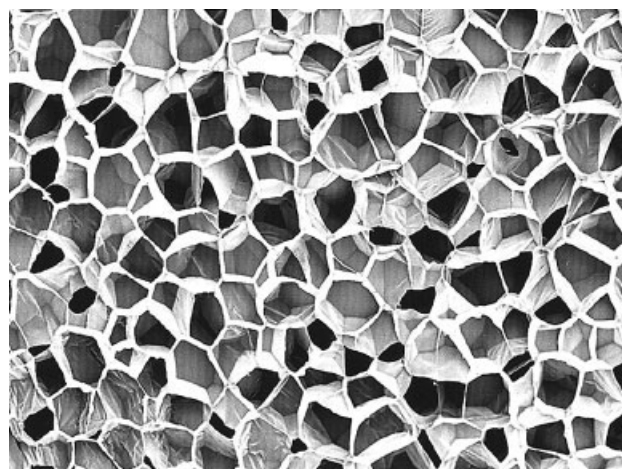
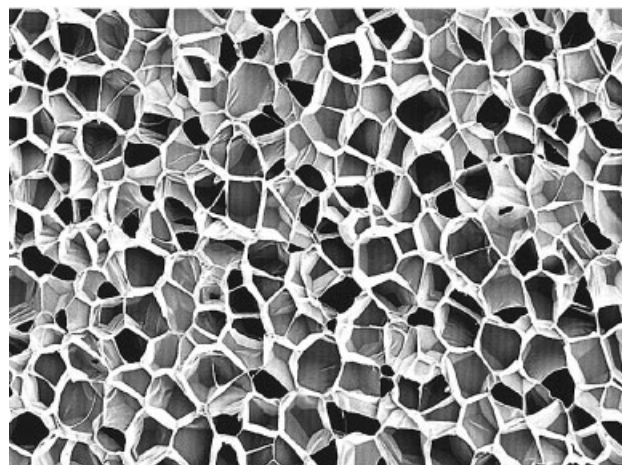


Figure 2 DSC thermograms of (a) sample EPS.01, (b) sample EPS.02, (c) sample EPS.03, and (d) sample EPS.04.



(a)



(b)

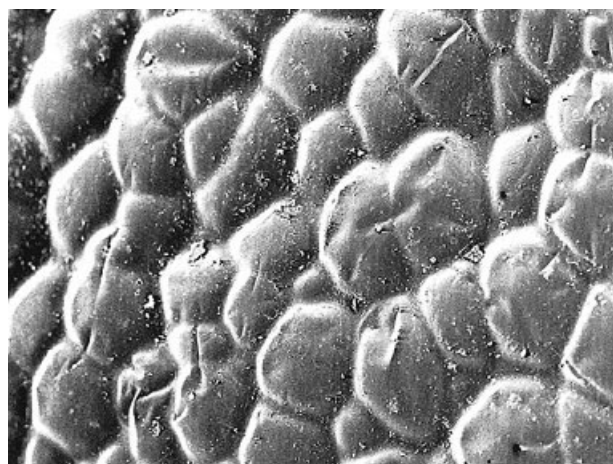
Figure 3 SEM micrographs of the inner parts of (a) sample EPS.01 (original magnification, 150 \times) and (b) sample EPS.04 (original magnification, 150 \times).

impurities coming from the styrene monomer were calculated from the areas under curves of the peak at 1.25 ppm to the peak coming from phenyl protons between 6.26 and 7.20 ppm. The results were 99% pure homo-polystyrene. The peak at 1.25 ppm was attributed [Fig. 1(b)] to the methyl protons of α -methylstyrene. The α -methylstyrene percentage in the copolymer was calculated from the aforementioned peaks by a consideration of the styrene homologue impurities in the starting styrene monomer. The calculated result confirmed the expected α -methylstyrene ratio in the CEPS.

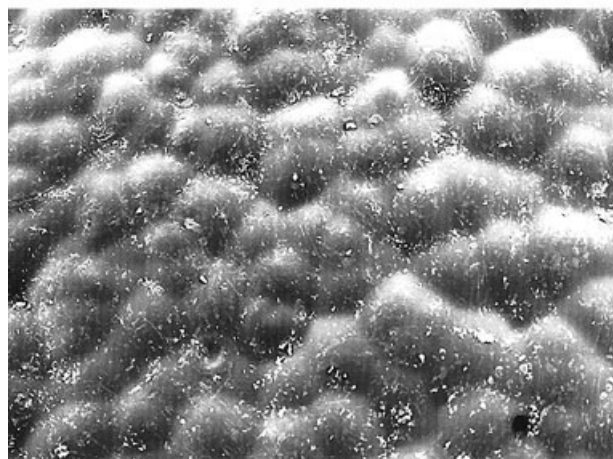
The DSC thermograms of the samples are given in Figure 2(a–d). The T_g value of the standard homopolymer [Fig. 2(a)] was 110.5 $^{\circ}$ C and the T_g values of 1.0, 2.5, and 5.0% α -methylstyrene-containing samples [Fig. 2(b–d)] were 110.8, 112.5, and 112.6 $^{\circ}$ C, respectively. The increase in the T_g values with an increase in the α -methylstyrene content was expected. The T_g

value of α -methylstyrene homopolymer was 170 $^{\circ}$ C, and through simple gravimetric calculations, it can be supposed that every additional percentage point of α -methylstyrene would cause an increase of approximately 1 $^{\circ}$ C in the T_g value. This estimation can be said to be true for the 1 and 2% α -methylstyrene-containing copolymers. However, the increase in the T_g value of the 5.0% containing copolymer did not fit 5 $^{\circ}$ C. This case can be explained by a lower than expected content of α -methylstyrene in the polymer chain due to the lower reactivity of α -methylstyrene in comparison with styrene.

SEM micrographs of the samples are given in Figures 3 and 4. Cross-sectional views of samples EPS.01 and EPS.04 are given in Figure 3(a,b), respectively. These figures show that the cell structures of the styrene homopolymer and copolymer were similar. The cell size and homogeneity of the cell sizes were also nearly the same. The outer surface of EPS appeared



(a)



(b)

Figure 4 SEM micrographs of the outer surfaces of (a) sample EPS.01 (original magnification, 200 \times) and (b) sample EPS.04 (original magnification, 200 \times).

rough [Fig. 4(a)]. However, the outer surface of CEPS [Fig. 4(b)] appeared smooth because of the existence of α -methylstyrene in the polymer structure. This indicated that the presence of the α -methylstyrene in CEPS prevented the collapse of the cell walls in EPS.

CONCLUSIONS

From the presented results, the following conclusions can be drawn: (1) the three expandable poly(α -methylstyrene-*co*-styrene) samples were prepared by suspension polymerization, (2) the thermal modification was achieved in this way, and (3) outer surface smoothness was attained by copolymerization with α -methylstyrene but only up to 5.0%.

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