Effect of Unsaturated Keto-Groups on Physico-Mechanical and Thermal Properties of Modified Polystyrene

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ABSTRACT: Polystyrene (PS), after polyolefins, is the most widespread polymer both in industry and daily life, successfully replacing some natural raw materials. In this study, as a serial of our previous study, modified polystyrene containing acetyl group (CH_3CO-) was used as a raw material and condensation reaction was performed in basic medium with aliphatic saturated and unsaturated aldehydes. The structures of modified polystyrenes with unsaturated keto-groups were investigated by chemical and spectral (FTIR vs. ^{1}H NMR) analyses. The effect of the functional groups bound to the structure of the polymer on physicomechanical and thermal properties of modified polystyrene was investigated. As a result, condensation products of modified polystyrenes with crotonaldehyde and cinnamaldehyde had higher physicomechanical properties and were more stable against the thermal destruction at high temperatures. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 1193–1202, 2011

Key words: polystyrene; modification; physicomechanical and thermal properties

INTRODUCTION

New polymeric materials with complex properties has recently become of great practical importance to polymer chemistry and plastic technology and moreover, can be synthesized through the polymerization of monomers or the chemical modification. There is a great interest in the last decade for the chemical modification of traditional polymers, with the aim of enhancing their chemical properties, making them useful for special applications. In recent years, the synthesis of polyfunctionalized polymers by chemical modification to increase their resistance against heat and their application areas have been developed continuously. Several studies on modifications of polymers have been reported.[1–6]

Polystyrene (PS) is commercially available polymer used extensively for low-cost applications. Chemical modified PS polymer with functional groups was expected to be a very desirable material. Functionalization of PS can be achieved by introducing other types of functional groups into the polymer or by modifying existed functional groups. There are only a few reports on discussing the modification of PS-based polymer, such as the ones including sulfonated PS,[7,8] brominated PS,[9] acetylated PS,[10] and maleated PS,[11,12] etc.

It was shown that new coating system with improved heat resistance, anticorrosive, and impact properties can be obtained by using modified PS.[13,14]

Since polymers containing unsaturated keto-groups have new light-sensitive property, they can be cross-bound by UV-rays.[15–19] Thus functionalization of PS by grafting reaction can be carried out either via the polymer backbone in the case of radical initiators or through the side phenyl rings using cationic catalysts. Acylation reaction of benzene ring was observed by Can et al.[20]

The reactions of PS ($M_n = 500 \times 10^3$) with maleic and acetic anhydrides, butadiene and isoprene in the medium of various Lewis acid catalysts ($BF_3 \cdot O(C_2H_5)_2$, $AlCl_3$, $ZnCl_2$, etc.) by one stage method were researched and modified polymers had good properties such as adhesion, corrosion resistance, photosensitivity, thermostability, and impact resistance.[21]

Modification of various molecular weight ($M_n = 230 \times 10^3 - 350 \times 10^3$) polystyrenes (PS) with maleic (MA) and acetic anhydrides (AA) in the medium of cationic catalysts $BF_3 \cdot O(C_2H_5)_2$ by one stage method was researched by Ahmetli et al.[22]

Thermal analysis is an important analytical method in understanding the structure–property relationship and thermal stability of composite materials. Literature reports several papers on thermal properties of styrene polymers.[23–28] Thermal properties of modified PS ($M_n = 350 \times 10^3$ and 500×10^3)

with maleic and acetic anhydrides and epichlorohydrin were investigated by us, too. It was determined that amount of functional groups bound to aromatic ring of polymer changes with moleculer weight of polymer and more functional groups were bound to the lower molecular weight polymer structure. PS modified by various modificators has more stability against thermal destruction than unmodified PS, depending on structure and amount of boound active polyfunctional groups to the aromatic ring. Polystyrenes with lower molecular weight are more resistant against thermal destruction.[29]

As seen from the above literature, polyfunctionalized polymer is an important subject in polymer chemistry. Therefore, this article deals with the study of the thermomechanical properties of modified polystyrenes with various keto-functional groups.

EXPERIMENTAL

Materials

Polystyrene (PS) ($M_n = 230 \times 10^3$), acetic anhydride (AA), acetaldehyde (AAld), propionaldehyde (PAld), crotonaldehyde (CrAld), benzaldehyde (BAld), 2-furaldehyde (FAld), cinnamaldehyde (CAld), $BF_3.O$ $(C_2H_5)_2$ cationic catalyst, 1,2-dichloroethane as solvent and KOH were purchased from Merck.

Synthesis of modified polystyrene (MPS)

Low molecular weight ($M_n = 230 \times 10^3$) PS was used for modification reaction by AA in the presence of cationic catalyst $BF_3.O(C_2H_5)_2$ in appropriate conditions. A reactor composed of mixer, cooler and thermometer was used in the experiments. 0.0125 mol acetic anhydride (AA) (25% of the polymer amount) was added to the solution of 0.05 mol PS in 60 mL chloroform by mixing. Then, modifier was dissolved completely, 0.0125 mol $BF_3.O(C_2H_5)_2$ was added drop-by-drop and the reaction was ended in 2 h at the temperature of 30°C. Modified PS was obtained without forming any by-product. The mixture was poured into a beaker and the modified PS was precipitated with methanol, dried in a vacuum oven at 50–60°C for 1h, weighed and analyzed. If there is unreacted anhydride in the medium, it does not precipitate with ethanol so it remains in the solution.[22]

Sensation reaction of MPS with various aldehydes

A reactor consisting of a mechanical mixer, cooler, heater, and thermometer was used in the experiment. Reactions were performed under various conditions such as MPS:aldehyde mole ratio being 1 : 0.5–1, aldehyde:catalyst mole ratio being 1 : 0.001–0.01 mol and temperature ranging from 20 to 40°C. We determined that most functional unsaturated keto-groups were bound under conditions such as MPS : aldehyde mole ratio being 1 : 1, aldehyde : catalyst mole ratio being 1 : 002, at 30°C and at pH 10–11.

Measurements and analyses

The acetyl and functional unsaturated keto-groups bound to the structure of the modified polystyrene were determined by chemical analysis.

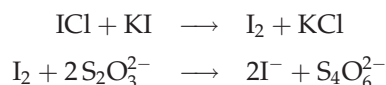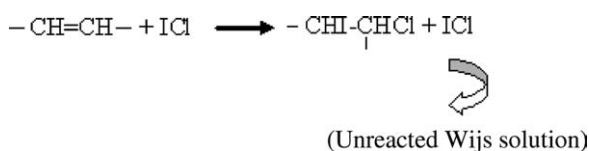### Determination of acetyl (-CO-CH₃) groups

The concentration of the acetyl group, bound to the structure of PS, was calculated by titration of acetic acid with 0.1N KOH, which occurred after the chemical modification reaction of PS with AA using $BF_3.O(C_2H_5)_2$ as catalyst.[29]

$$\text{AA, mol/L} = (\Delta V.T_{KOH}.1000)/56.1 \times 2$$

where, ΔV is the volume of 0.1N KOH used for titration of acetic acid in 1 mL sample (mL), T_{KOH} is the amount of KOH in 1 mL 0.1N KOH solution (0.005208 g), 56.1 is the molecular weight of KOH (g).

Determination of double bonds

The number of double bonds (iodine value) in polymer was determined by titration method. It is expressed as the "number of grams of iodine that will react with the double bonds in 100 g of sample." The determination is conducted by dissolving a weighed sample (approximately 0.2 g) in a 10 mL nonpolar solvent such as CCl_4, then adding 20 mL of iodine monochloride in glacial acetic acid solution (Wijs solution). After completion of the reaction, the excess iodine monochloride is decomposed to iodine by the addition of 10 mL aqueous 15% potassium iodide solution, which is then titrated with standard 0.1N sodium thiosulfate solution.

$$-CH=CH- + ICl \longrightarrow -CHI\text{-}CHCl + ICl$$

(Unreacted Wijs solution)

$$ICl + KI \longrightarrow I_2 + KCl$$
$$I_2 + 2\,S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$

the iodine value (I.V.) was calculated by using the following equation:

$$\text{I.V.} = \frac{(V_1 - V_2) \times 0.012697}{m} \times 100$$

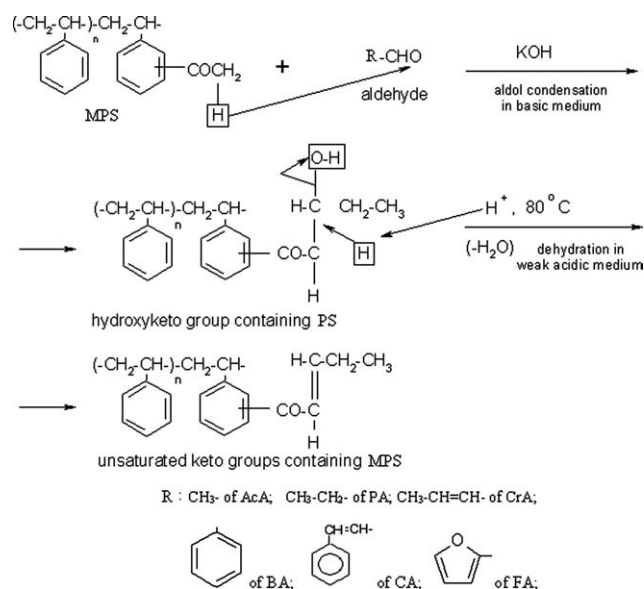**Figure 1** Scheme of condensation reaction of MPS with aldehyde.

where, V_1 is the volume of 0.1N $Na_2S_2O_3$ used for control titration (mL), V_2 is the volume of 0.1N $Na_2S_2O_3$ used for titration with sample (mL), 0.012697 is the amount of iodine corresponding to 1 mL of 0.1N $Na_2S_2O_3$ (g), m is the amount of polymer sample (g).[30]

Thermal analysis

The thermal analysis experiments were performed with a NETZCH-Geratebau GmbH model thermogravimetric analyzer. Samples were heated under nitrogen atmosphere from 250 to 500°C at a heating rate of 10°C min^{-1}. CEAST HDT-VICAT test equipment was used for measuring softening point.

Mechanical testing

MPS specimens were prepared in stainless-steel molds using a hydraulic press at a temperature of 180°C and a pressure of 50 MPa. The thickness of the specimens was ∼ 4 mm. Physicomechanical properties as endurance against stretch (kg/mm^2; N/mm^2) and relative extension (mm; %) were performed by stretch-pressure test equipment (TST-Mares/TS-mxe) and hardness was measured by Shore Durometer TH 210.

Spectral analysis

The FTIR spectra were recorded with a Unicam SP 1025 spectrometer. ^{1}H NMR spectra were performed on Varian 400-MRBruker Avance DPX-400 at 400.13 MHz and 25°C. Sample was dissolved in CDCl$_3$.
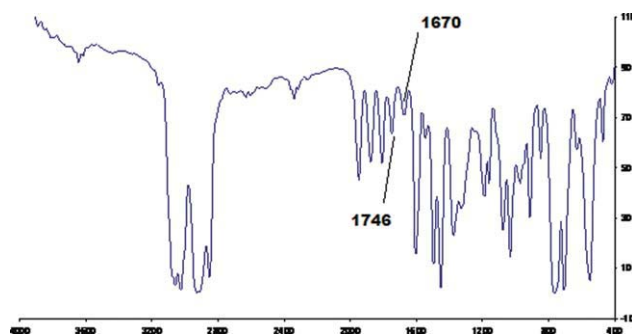

Figure 2 FTIR spectrum of MPS containing —CO—CH=CH—CH3 group. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS

Since more acetyl (-CO-CH$_3$) groups (14.6% mole) were bound the low molecular weight (M_n = 230,000) PS, this MPS was used as a raw material in study. Sheme and mechanism of condensation reaction of MPS with aldehydes is shown in Figure 1. As a result of condensation reaction of MPS with aliphatic and aromatic aldehydes, different unsaturated keto-groups bound to the polymer's aromatic ring bring higher physicomechanical and thermal properties to MPS.

The structure of synthesized MPSs with keto groups was characterized by FTIR-spectroscopy as indicated in Figures 2 and 3. The analysis of the FTIR-spectroscopy results helped for the evaluation of chemical composition of the MPSs. FTIR spectra have peaks at 1746, 1763 cm^{-1} indicating C=O group of ketone and 1678, 1670 cm^{-1} indicating trans C=C bond, respectively. When Figure 2 was compared with the FTIR-spectrum of reaction product of the MPS with crotonaldehyde, it was observed that existence of more longer peak at 1678 cm^{-1} indicated dien characterized bond (Fig. 3). All peaks indicated that MPS was reacted with aldehydes.
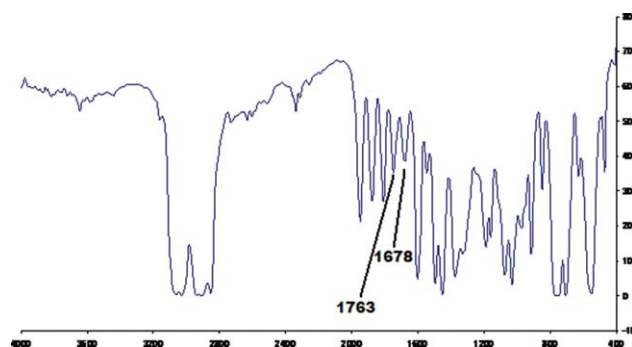

Figure 3 FTIR spectrum of MPS containing —CO—CH=CH—CH=CH—CH3 group. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
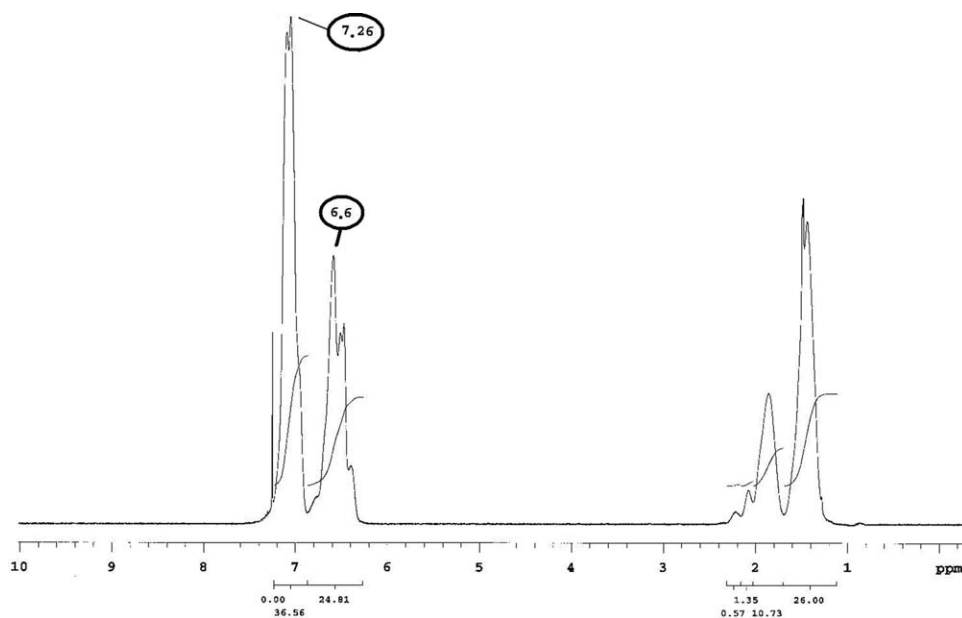
Figure 4 ^{1}H NMR spectrum of PS.

Figures 4 and 5 show ^{1}H NMR spectra of the unmodified and modified PS, Figures 6 and 7 show MPSs with unsaturated keto group in CDCl$_3$. The small peak at 7.26 ppm in all of the ^{1}H NMR spectra results from the solvent, CDCl$_3$. For the spectra of the polymers shown in Figure 4, a single peak as well as double peaks at around δ 6-6.6 ppm was found, attributed to the characteristic signals of hydrogen of aromatic benzene ring. Besides, it was shown in Figure 5 that the signal at around δ 2.6 ppm was assigned to

methyl protons of ─COCH$_3$ group of PS. In the spectrum of MPS containing (─CO─CH═CHvCH$_3$) unsaturated keto-group, the signal slides from δ 2,6 to δ 2,3 because of the methyl proton's slide (Fig. 6). In the spectrum of MPS containing (─CO─CH═CH─CH ═CH─CH$_3$) unsaturated keto-group, the signal slides to more longer peak from δ 2,6 to δ 2,35 because of the CH proton's slide (Fig. 7).

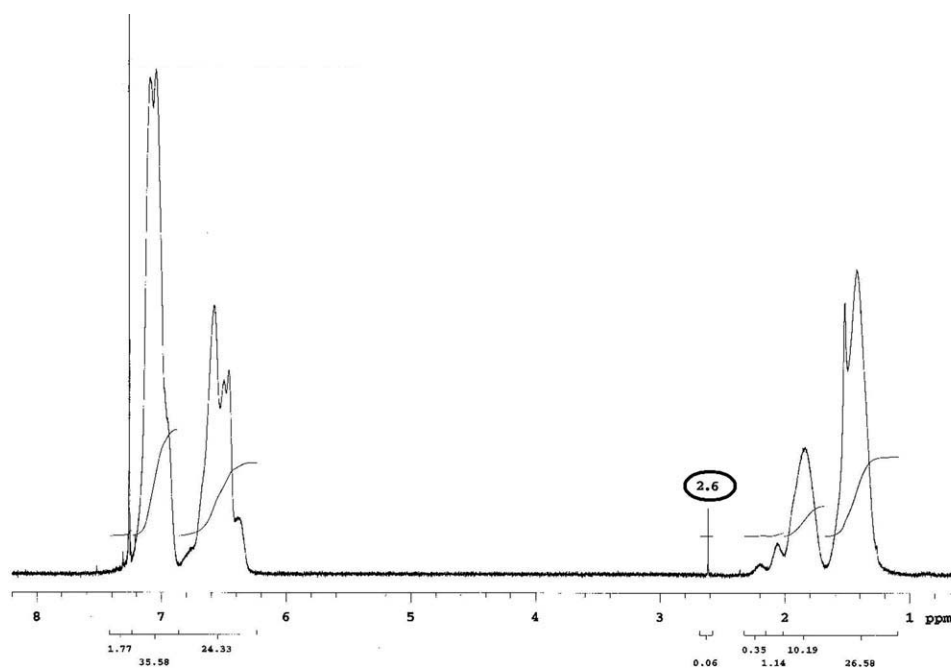According to Wijs method, iodine values of MPSs containing unsaturated keto-groups are shown in

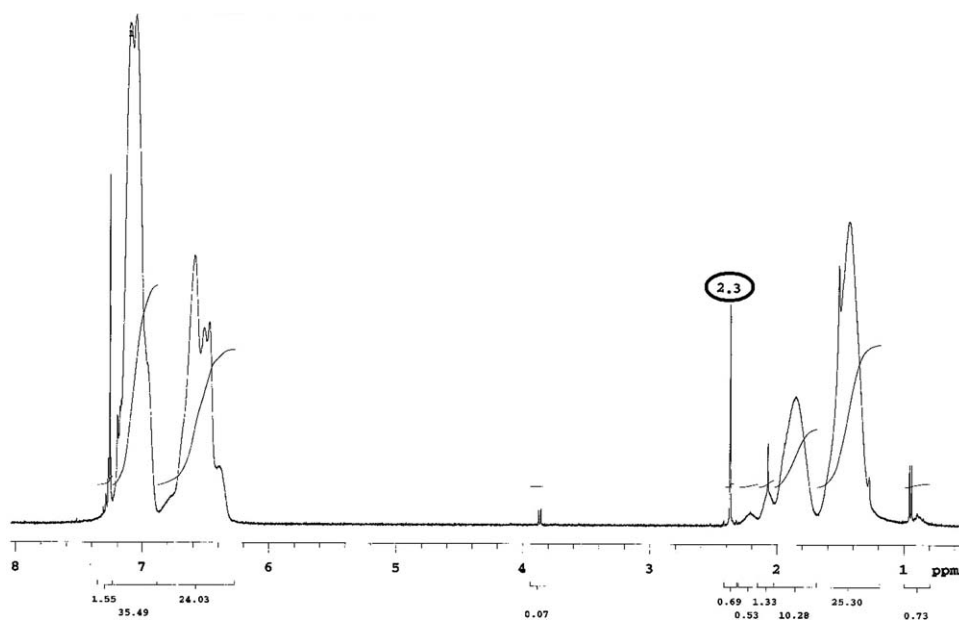**Figure 5** ^{1}H NMR spectrum of PS containing ─COCH3 group.

Figure 6 ^{1}H NMR spectrum of MPS containing —CO—CH=CH—CH3 group.

Table I. As seen from Table I, they have different iodine values. Among the condensation products, MPSs with CrAld and CAld have higher iodine value depending on double unsaturated bonds in their structure. Iodine values of these compounds were 190.35 and 154.97, respectively. These results showed that the reaction was progressed by connecting unsaturated keto-groups.

Thermal analysis is an important analytical method in understanding the structure–property relationships and thermal stability of polymers. Literature reports several papers on pyrolysis of plastics. Thermal degradation of polymers occurs through random and chain degradation (depolymerization reaction) initiated by thermal and UV light.[31] The depolymerization reaction in thermal degradation does not need to be initiated at terminal end of the macromolecule, instead, imperfections in the chain structure (initiator fragment or a peroxide or ether link) form a weak link from where depolymerization starts. A large number of addition polymers depolymerizes at elevated temperatures.[32] Thermal degradation above 200°C leads to chain scission and largely depends on impurities like unsaturation
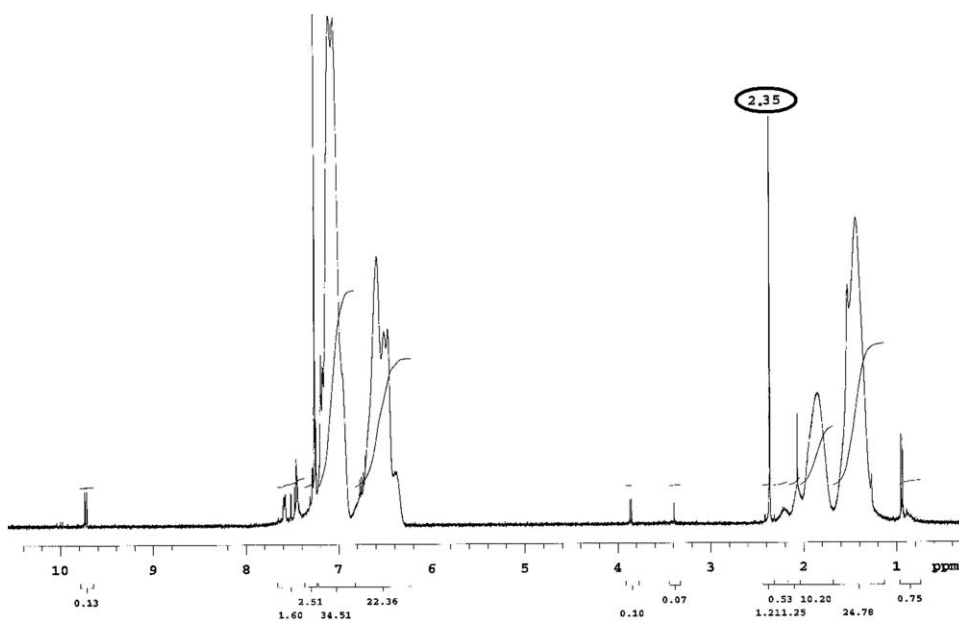

Figure 7 ^{1}H NMR spectrum of MPS containing —CO—CH=CH—CH=CH—CH3 group.

TABLE I
Iodine Values of Various Unsaturated Keto-Groups Containing MPSs

MPSs	Iodine value
PS-CO-CH=CH-CH$_3$	88.83
PS-CO-CH=CH-CH$_2$-CH$_3$	133.24
PS-CO-CH=CH-CH=CH-CH$_3$	190.35
PS-CO-CH=CH-[phenyl]	142.28
PS-CO-CH=CH-CH=CH-[phenyl]	154.97
PS-CO-CH=CH-[furan with O]	127.1

sites, head-to-head units, etc.[33] PS thermally gets degraded into organic compounds such as phenol, quinine, naphthalene, and diphenylamine at the experimental temperature of 350–450°C.[34–37] The mechanism of thermal degradation of polymers is an interesting subject, not only from fundamentals of polymer reactions' point of view but also in understanding heat-resisting characteristics, polymer processes such as extrusion or injection molding, and the effective utilization of plastic wastes. The thermal degradation of polymers consisted of two distinct reactions: one is a random scission of links, causing a molecular weight reduction of the raw polymer, and the other is a chain-end scission of C—C bonds, generating volatile products. α-substituted vinyl polymers which degrade mostly through the process of depolymerization have been converted to their respective monomers almost quantitatively.[38] The chain-end scission takes place at the gas-liquid interface in the working reactor.[39] The thermal degradation of poly(o-propionylstyrene) (POPS) was studied at 385°C under high vacuum by Weir et al. The principal reactions were removal and decomposition of the propionyl substituents, depolymerization, oligomer formation, and chain scission. While the mechanism of degradation is qualitatively similar to that of poly(styrene), the probability of transfer reactions occurring with the polymer is considerably greater, on account of the presence of ethyl and methyl radicals (derived from the propionyl groups).[40] The thermal degradation of poly(vinylacetophenone) (PVAP) was studied at 380°C under high vacuum. The principal reactions were removal and decomposition of acetyl group depolymerization and random chain scission, as evidenced by the pattern of number average molecular weight changes. The resulting chain radicals undergo β-scission (the principal mode of chain scission) to yield a terminally unsaturated molecule and a macro radical. These two species further decompose to give oligomeric products and monomer.[41] Weir et al. investigated the thermal degradation of poly(α-D-vinyl acetophenone) at 420°C under high vacuum too. Principal reactions were depolymerization, random chain scission, and the elimination of the acetyl ring substituent.[42] The thermal degradation characteristics of the two polystyrene polymers over a range of 280–350°C temperatures were investigated by Howel et al. It was determined that at low temperature, i.e., 280°C, the predominant process would seem to be chain unzipping to form styrene monomer. At higher temperatures (>300°C), degradation probably involves

TABLE II
Effect of Unsaturated Keto-Groups on Thermal Properties of MPSs

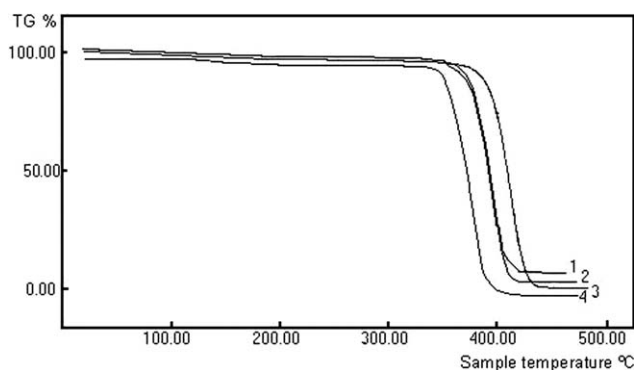| MPS with unsaturated keto group	Loss of weight, %				Residual weight (%) 500°C
	300°C	350°C	400°C	420°C	
PS-CO-CH=CH-CH$_3$	4	5	23	75	5
PS-CO-CH=CH-CH$_2$-CH$_3$	3	5	20	75	4.8
PS-CO-CH=CH-CH=CH-CH$_3$	2	3	15	73	5.85
PS-CO-CH=CH-[phenyl]	4	10	15	81	6
PS-CO-CH=CH-[furan with O]	5	12	10	74	10
PS-CO-CH=CH-CH=CH-[phenyl]	2	3	6	61	11
PS –COCH$_3$	2	3	25	80	0
Unmodified PS	0	0	35	85	0

Figure 8 TGA curves of condensation products of MPS with: 1-AAld; 2-PAld ; 3-CrAld and 4-MPS.

significant random chain scission.[43] The thermal degradation of poly(p-methylstyrene) was studied in the temperature range of 300–400°C by Murakata et al.[44] The thermal degradation of polystyrenes substituted with chloromethoxyphosphonated groups was studied in the temperature range of 280–430°C by Camino et al.[45]

As seen from literature, the thermal degradation of PS based polymers was studied generally not above 450°C. In our study, the effect of the polymer structure on thermal properties was investigated by TGA analysis in the temperature range of 50–500°C and results are given in Table II and Figures 8 and 9. The nature of the substituents played an important role in the thermal stability. According to our research, MPSs modified by various aldehydes have more stability against thermal destruction than unmodified PS, depending on structure of active polyfunctional groups bound to the aromatic ring. In all TGA curves of MPSs, contrary to PS, two stages of weight loss were observed and the

first was in the range of 125–150°C involving the loss of about 5% of the total mass. It can be assigned to the elimination of water adsorbed by the hydrophilic polymer, the second with fragmentation of the polymer. The thermograms show that the second degradation temperature (SDT) of all polymers was above 350°C. The products of the second stage are the typical aromatic materials which arise from the degradation of polystyrene.[46] Styrene was the major product of degradation and the most important minor products were benzene, ethyl benzene and toluene.[47] The high SDT of MPSs with unsaturated keto groups indicates good thermal stability compared to MPS and unmodified PS. We can explain this result as follows: at high temperature, $-CH=CH-$ groups cross-bond and increase stability of polymer against thermal destruction. Cullis and Laver reported in their study that thermogravimetric curves for the degradation of carboxy-terminated polybutadiene showing the free-radical crosslinking and cyclization reactions cause an increase in the thermal stability of the polymer during degradation.[48] As compared with MPSs with $-CO-CH=CH-CH_3$ and $-CO-CH=CH-CH_2-CH_3$ groups, it was determined that carbon number of aliphatic keto groups affected thermal properties at higher temperatures (>350°C). The thermal stability of MPSs was rised with increasing n, that is, the length of alkylene side chain. Similar result was obtained for MPSs with aromatic keto-groups. This result is compatible with Zuev et al. study.[49] It was determined by us that MPSs with double unsaturated bonds are more stable against thermal destruction than other MPSs. The onset temperature of the second main degradation stage as well as temperature
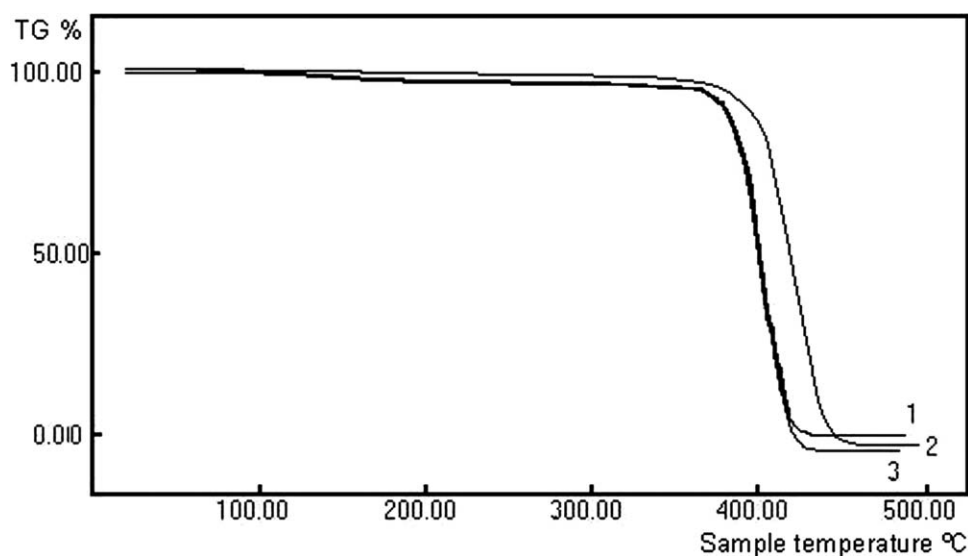

Figure 9 TGA curves of condensation products of MPS with: 1-FAld; 2-CAld; 3-Bald.

TABLE III
Effect of Unsaturated Keto-Groups on Physico-Mechanical Properties of MPSs

MPSs	Tensile strength		Elongation at break		Softening point by Vicat	Hardness by Shore Durometer
	kg/mm^2	N/mm^2	mm	%	°C	HD
PS-CO-CH=CH-CH$_3$	3.48	34.11	1.94	1.76	73.8	86.92
PS-CO-CH=CH-CH$_2$-CH$_3$	3.14	30.75	1.49	1.35	72.9	84.37
PS-CO-CH=CH-CH=CH-CH$_3$	4.18	41.02	2.16	2.91	77.4	84.82
PS-CO-CH=CH-C$_6$H$_5$	2.99	29.32	1.36	1.14	75.7	83.46
PS-CO-CH=CH-(furan)	2.53	24.77	1.43	1.28	71.2	83.3
PS-CO-CH=CH-CH=CH-C$_6$H$_5$	3.74	36.66	2.03	1.86	69.0	85.0
PS-CO-CH$_3$	2.13	23.86	1.05	0.93	76	87.5
Unmodified PS	1.60	15.67	0.70	0.42	80	89.0

of maximum degradation for polymers decreases with polymer unsaturation. Maximum decomposition temperature of MPSs with aliphatic keto groups changed between 445 and 450°C, with aromatic keto groups, the change was between 455 and 460°C. The amount of residual weight at the end temperature of MPSs with aromatic keto groups was higher than other MPSs and unmodified PS. As a result, if we inspect the effect of keto group structure, like aliphatic or aromatic group on destruction, the best thermal result was obtained for MPS containing —CO—CH=CH—CH=CH—C$_6$H$_5$ group.

Table III presents detailed information related to softening points of polymers. The results show that MPSs containing unsaturated keto-groups have no remarkable differences on their Vicat softening temperatures. Properties such as the chain elasticity, side group, branching, cross-bond, and mole weight in polymers affect the temperature of softening. Glassy transition temperature of polymers having elastic chains is lower than polymers having hard chains.[50] According to Table II, bonding of unsaturated keto-group to the structure of PS provided elasticity for PS and elongation value at the time of rupture increased from 0.42% to 2.9%. On the other hand, since branching in chains limits approaching of chains and increases the volume, softening temperatures of branched polymers are lower than those of linear structures.[50] When MPSs having aliphatic and aromatic keto-groups are compared, they have lower softening temperatures due to the steric volume of the aromatic group. Because of these results,

as compared with all MPSs with keto-groups having unmodified PS, they have lower Vicat softening points.

The mechanical properties of polymers are influenced by molecular weight, crosslinking, branching, segmental motion, morphology, and external conditions such as temperature, pressure, loading rate, environmental condition, extent of compound, etc.[50–54] The structure of the side-chain substituents on the polymer backbone is a major compositional factor impacting polymer functionality. Important aspects of substitution are the chemical structure of the substituents, the extent of backbone substitution, and the uniformity of substitution. The nature of the side chain substituent type also significantly impacts mechanical properties. Increasing the amount of highly polar, ionic side-chains tends to result in an increased tensile strength.[55] The effect of side group structure on the compressive strength of novel biodegradable polyphosphazene based polymers was investigated by Sethuraman et al. Results of mechanical testing studies demonstrated that the nature and the ratio of the pendent groups attached to the polymer backbone play a significant role in determining the mechanical properties of the
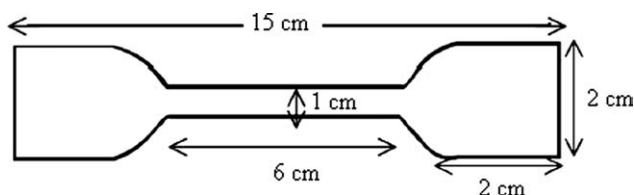

Figure 10 Dumb-bell shape of MPS specimens.

resulting polymer. The compressive strength of polymer with aliphatic alanine side group was significantly higher than polymers with aromatic alanine groups.[56]

To investigate physicomechanical properties, such as tensile strength, elongation at break and hardness of the MPSs, mechanical testing was performed. The dumb-bell shape of the MPSs specimens with proper dimension is shown in Figure 10. The results are given in Table III. It was determined that physicomechanical properties of synthesized MPS with unsaturated keto-groups changed depending on its structures too. As shown in Table II, reaction product of MPS with CrAld which has double unsaturated bond and more carbon number ($-CO-CH=CH-CH=CH-CH_3$) has higher tensile strength and elongation data than MPSs with other aliphatic and aromatic keto-groups. As a result of condensation reaction, tensile strength of MPS changed from 23.86 N/mm^2 to 41.02 N/mm^2 and elongation at break changed from 0.93% to 2.91%. If these results were compared with data obtained for MPSs with aromatic keto-groups, MPSs with aliphatic keto-groups has higher physicomechanical properties. Among the MPSs with aromatic keto-groups, MPS which has more carbon number and double unsaturated bond showed similar results. Physicomechanical properties of this MPS were higher than other MPSs with aromatic groups. Tensile strength was 36.66N/mm^2 and elongation at break was 1.86% for MPS with $-CO-CH=CH-CH=CH-C_6H_5$ group. As a result, the bonding to aromatic ring of PS unsaturated keto-groups instead of $-CO-CH_3$ group significantly improved some physicomechanical properties of unmodified PS and MPS.

Hardness is not a reliable measure of stiffness. Hardness measurements derive from small deformations at the surface, whereas stiffness measurements such as measurement of tensile modulus derive from large deformations of entire mass. Unlike with metals, there is no correlation between hardness and tensile strength of elastomers. As the hardness increases, the tensile strength of an elastomer may increase to a maximum then decrease, or it may decrease from the beginning, depending on the formulation of the compound.[57] As seen from Table II, results which were obtained for hardness of MPSs did not contain remarkable differences. This result can be explained by the low mole % of keto-groups bound to the aromatic ring of PS which were ineffective on molecular weight of PS.

CONCLUSION

Condensation reaction of PS containing acetyl group with aliphatic and aromatic aldehydes was performed. Thermal decomposition was occurred within the temperature range of 50–500°C. Synthesized MPSs with double unsaturated keto-groups such as MPSs with CrAld and CAld are more stable against thermal destruction and have higher physicomechanical properties than other MPSs. MPSs with unsaturated keto-groups show a significant increase in elongation at break and thermal stability compared with MPS and unmodified PS.

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