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THERMAL BEHAVIOR OF POLYSTYRENE SYNTHESIZED IN THE PRESENCE OF CARBOXYMETHYL CELLULOSE

A. F. Naves, Priscila M. Kosaka, J. R. Matos and Denise F. S. Petri[*]

Instituto de Química, Universidade de São Paulo, Av. Prof Lineu Prestes 748, 05508-900 São Paulo, SP, Brazil

Thermal analysis of polystyrene (PS) particles synthesized in the presence of cetyltrimethylammonium bromide (CTAB) and carboxymethyl cellulose (CMC), with the degree of substitution 0.7 and average molecular mass ($\overline{MM}$) of 90000 and 250000 g mol^{-1} was carried out. PS chains grown in the presence of CMC having $\overline{MM}$ of 90000 g mol^{-1} presented glass temperature (T_g) at 375 K, which is in agreement with the literature value. However, the PS chains grown in the presence of longer CMC chains ($\overline{MM}$ = 250000 g mol^{-1}) presented T_g at 352 K. This 23 K decrease in the T_g value was caused by the increased polydispersity, which was confirmed by gel permeation chromatography. Thermogravimetry showed five mass loss steps between 298 and 873 K.

Keywords: *carboxymethyl cellulose, DSC, emulsion polymerization, polydispersity, polystyrene, TG/DTG*

Introduction

Polymeric latex particles are widely used in the paint industry and in the development of devices used in biotechnology [1]. When polymeric latex films formed onto solid substrates are annealed at temperatures higher than their glass transition temperature, the films may become unstable and dewetting takes place [2, 3]. If there are van der Waals type interactions between substrate and polymer, the values of the Hammaker constant A for polymer/polymer and polymer/substrate are representative for the film stability. If $A_{\text{polymer/polymer}}$ is higher than $A_{\text{polymer/substrate}}$, dewetting will be favored [2, 3]. Moreover, the formation of a stable film requires the homogeneous melt from coalescence of polymeric particles [4, 5]. The determination of T_g values and the particle composition are very important representatives for the polymeric film formation. When the film formation takes place well above its T_g, evaporation is the rate-limiting step and particle coalescence occurs simultaneously with water evaporation. At temperatures closer to T_g, particle deformation is the rate-limiting and the loss of water leads to the deformation of voids that shrink slowly over time [5]. Therefore, studying the thermal behavior of polymeric particles is very important to assure the success in the industrial applications.

Polystyrene (PS) particles are commonly synthesized by emulsion polymerization using large amounts of surfactant as emulsifier, which are released to the wastewater causing environmental problem. In this work, PS particles were polymerized in complexes formed by tiny amounts of cetyltrimethylammonium bromide (CTAB), a cationic surfactant, and carboxymethyl cellulose (CMC), a natural polyanion [6]. This procedure combines the advantage of synthesizing and stabilizing particles with carboxylate groups on the surface in a one-step method using very small amounts of surfactant, decreasing the environmental pollution [7]. Typical recipes [8] of emulsion polymerization yield high molecular mass polymer chains. Recently Sanchez *et al*. [9] showed that decreasing the PS molecular mass the glass temperature decreased down to 22 K, because the concentration of end-groups increased, favoring the dynamics of the co-operative conformational rearrangements of the chain segments. In the present work the thermal behavior of PS synthesized in the presence of CTAB and CMC was investigated by means of DSC and TG/DTG techniques and the results were completed with gel permeation chromatography (GPC) experiments.

Experimental

Materials

Styrene (S, Aldrich, S497-2), cetyltrimethylammonium bromide (CTAB, Aldrich, USA), potassium persulfate ($K_2S_2O_8$, Merck, Germany) and carboxymethyl cellulose (CMC, Aldrich, USA), sodium salt with an average degree of substitution (DS) 0.7 and $\overline{MM}$ of 90000 g mol^{-1} (CMC-90) and $\overline{MM}$ of 250000 g mol^{-1} (CMC-250) were used in the polymerization.

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[*] Author for correspondence: dfsp@iq.usp.br

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Synthesis of PS

The synthesis of PS particles followed a typical emulsion polymerization recipe [8], except that instead of water, the medium was a solution of CMC. CTAB was added to 70 mL of aqueous solution of CMC at the concentration of 1.0 g L^{-1}, so its final concentration was $0.25 \cdot 10^{-3}$ mol L^{-1}. The medium was purged with N_2 for 30 min, while the temperature was kept at (355± 2) K. Afterwards 0.009 g of $K_2S_2O_8$ initiator, and then 2 min later the monomer was added to the system keeping the [CTAB]:[S]=$9.1 \cdot 10^{-4}$:1 surfactant to monomer molar concentration ratio. The polymerization was carried out under reflux and stirring. After three hours the system was cooled down to room temperature and dialyzed (dialysis membrane 14000 *MM*, Viskase Corporation, USA) during four days changing 4 times per day the water. No buffer was used in this process. The pH of the dialyzed dispersions was between 4.5 and 4.8. The hybrid particles were identified as PS/CMC-90 and PS/CMC-250. The synthesis of hybrid particles is reported elsewhere [7].

Characterization of PS

The particles were dried at 333 K reaching constant mass. DSC curves were recorded using a Shimadzu DSC-50 cell, Al crucibles and about of 6 mg samples, under dynamic nitrogen atmosphere (50 mL min^{-1}) at a heating rate of 10 K min^{-1} in the temperature range of 298–403 K. After heating the samples were left to cool down spontaneously to 298 K. After then the sample was reheated under the same conditions. The second heating curves were used to determine the T_g. The DSC cell was calibrated with In (*m.p.* 430 K; ΔH_{fus}=28.54 J g^{-1}) and Zn (*m.p.* 693 K). TG/DTG curves were obtained with a Shimadzu model TGA 50 thermobalance in the temperature range of 298–873 K, using Pt crucibles and about 4 mg of samples, under dynamic nitrogen atmosphere (50 mL^3 min^{-1}) at heating rate of 10 K min^{-1}.

The dried particles were dissolved in tetrahydrofuran (THF) at the concentration of 1 g L^{-1} and filtered through a PTFE membrane (Roth, Germany, 0.45 μm pore diameter). Adding ethanol to the filtrate, it turned turbid, indicating the presence of PS, while undissolved CMC remained on the filter. A new aliquot of filtrate was prepared and analyzed by gel permeation chromatography (GPC) in a LC-10AD Shimadzu equipment, using UV spectrophotometer and refractometer as detectors. PS G5000, G4000 and G3000 Progel TKS (Supelco) columns were used for the calibration.

The zeta potential values were determined for the PS/CMC-90 and PS/CMC-250 particles in a ZetaPlus-Zeta Potential Analyzer (Brookhaven Instruments Corporation, Holtsville, NY) equipped with a 677 nm laser. The measured values amounted to –(55±5) mV, evidencing the presence of CMC carboxylate groups on the surface [7].

Results and discussion

The DSC measurements on PS/CMC-90 and PS/CMC-250 are shown in Fig. 1. The values determined for T_g are 375 and 351 K, respectively. For the sake of comparison, a commercial PS (BASF, Ludwigshafen) sample presented T_g at 365 K. Table 1 shows the onset, endset and mid point values determined from DSC curves for PS/CMC-90, PS/CMC-250 and commercial PS. The behavior of PS with CMC-90 is comparable to that of the commercial PS has and both they are in a good agreement with the literature values [9, 10], where the reported T_g values are between 363–383 K. However, the T_g found for PS/CMC-250 is 23 K lower than that was found for PS/CMC-90, similarly to Sanchez *et al.*'s findings [8], where a decrease in the $\overline{MM}$ of PS from 600000 to 4000 g mol^{-1}, was reported while the T_g was decreased with 22 K. When the concentration of the end-groups increased, the dynamics of the co-operative conformational rearrangements of the chain segments was favored. An end group generates a larger free volume than a monomeric unit does. Therefore, the increase in the free volume fraction decreased the glassy transition. Moreover, packing and size distribution might also influence the free volume. The obtained results indicate that PS chains reached in the presence of CMC-250 are probably shorter and/or more polydisperse than the PS chains with CMC-90. These are very important parameters concerning to the polymeric film formation.

GPC measurements have been performed in order to determine the molecular mass distributions for the PS chains grown in the presence of CMC-90 and CMC-250. Figures 2 and 3 show the GPC curves obtained in the presence of CMC-90 and CMC-250, re-

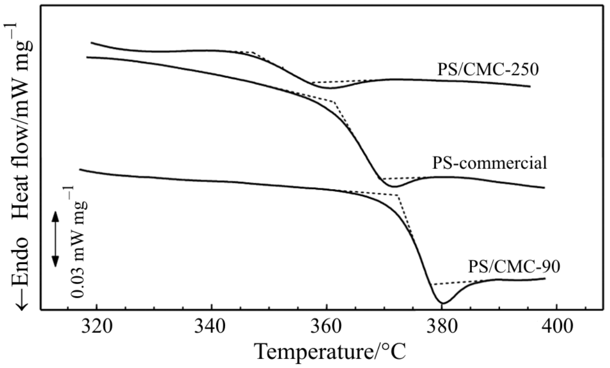

Fig. 1 DSC curves of PS/CMC-90, PS/CMC-250 and PS commercial samples

Table 1 Onset, endset and mid point values determined from DSC curves for PS/CMC-90, PS/CMC-250 and commercial PS

Sample	Onset/K	Endset/K	Mid point/K
PS/CMC-90	372.4	377.9	375.2
PS/CMC-250	347.2	356.8	352.4
PS-commercial	361.3	369.2	365.6

spectively. In both cases they are multimodal. In the low molecular mass range the M_w/M_n ratios provide the higher polydispersity of PS chains grown in the presence of CMC-250. In the opinion of the authors this should be the responsible for the observed decrease in the T_g values. In the high molecular mass range, the M_w/M_n ratios obtained for PS/CMC-90 and PS/CMC-250 are similar, indicating that the CMC chain length has no effect on the average molecular masses of PS. The peak areas corresponding to the low molecular mass fractions are about 52 and 54% of the total area for PS/CMC-90 and PS/CMC-250, respectively, and are probably composed by non-reacted monomers, non-reacted surfactants and very short oligomers.

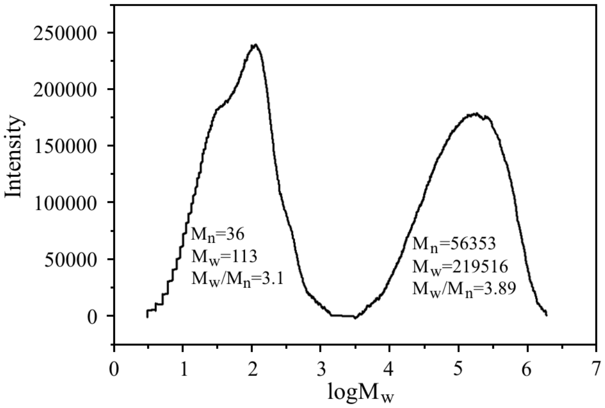

Fig. 2 GPC analysis of PS/CMC-90

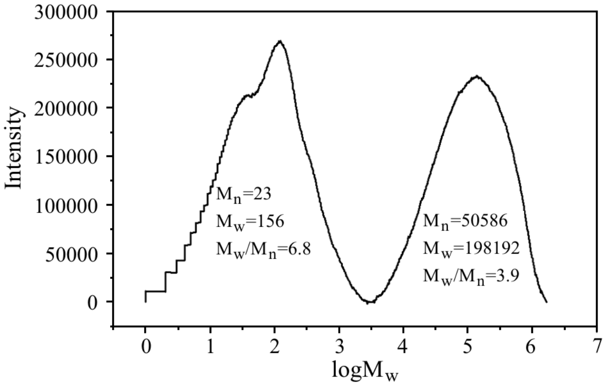

Fig. 3 GPC analysis of PS/CMC-250

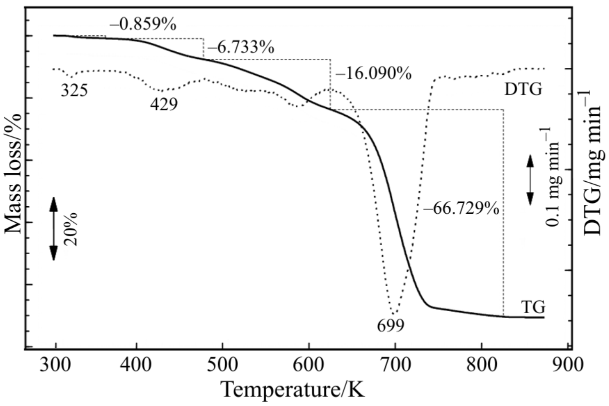

Fig. 4 TG/DTG curves of PS/CMC-250

During the initial stages of the polymerization the monomer concentration in the latex particles is controlled by thermodynamic parameters, as the interfacial tension γ, between latex particles and the aqueous medium and the Flory–Huggins parameter χ [8]. Calculations done for a styrene emulsion at 323 K, with χ=0.45 and γ=20 mN m^{-1}, showed that the monomer concentrations are about 55 and 62% of the concentration of pure monomer for particles with mean radii of 50 and 100 nm, respectively. At the end of the polymerization, the concentration of residual monomer depends on the initiator efficiency. Persulfate efficiency lies typically at 3%, generating about 5% of residual monomer in the particles [8]. The monomer content in the particles was determined by thermogravimetric analysis. The TG/DTG curves of PS/CMC-250 (Fig. 4) presented five mass loss stages. The steps belonging to the DTG peaks with 325 and 429 K peak temperatures correspond to a mass loss which is due to polymerization residues and non-reacted monomer evaporation [10]. The latter mass loss is about 6.7%, which is slightly larger than the residual monomer content found in the traditional styrene emulsion polymerization. This finding shows that the presence of the hydrophilic CMC does not represent a barrier for the hydrophobic monomer. The mass losses between 478 and 624 K correspond to the thermal decomposition of CMC [6] and oligomers, with a mass loss of 16.1%. The step belonging to the 699 K DTG peak was attributed to the decomposition of PS [10]. The few residual surfactant molecules are probably decomposed together with the PS chains.

Conclusions

DSC and TG/DTG curves were recorded for PS particles polymerized in aqueous complexes of CMC and CTAB. DSC measurements showed upon increasing the CMC molecular mass the resulting PS chains turned more polydisperse, especially in the low molecular mass range, as evidenced by the decrease in the T_g with 23 K. These findings were corroborated with the GPC analysis. TG/DTG curves were very important to quantify the amounts of (*i*) residual monomer, (*ii*) CMC and oligomers and (*iii*) PS chains in the particles. These parameters are essential for applying the hybrid PS/CMC particles in the thin film technology.

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