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Thermal stability of poly(styrene-b-methyl methacrylate) and poly(styrene-b-ethylene-co-1-butene-b-methyl methacrylate)

A gel permeation chromatographic study

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Summary

The thermal stability of poly(styrene-b-methyl methacrylate) diblock copolymers (= P(S-b-MMA)) and poly(styrene-b-ethylene-co-1-butene-b-methyl methacrylate) triblock copolymers (= P(S-b-EB-b-MMA)) was investigated. Well-defined high molecular weight block copolymers with narrow molecular weight distribution (MWD) were molded at different temperatures in vacuum and the alteration of the MWD was sensitively monitored by gel permeation chromatography (GPC). Up to 240°C P(S-b-MMA) shows almost no broadening of the MWD. At higher temperatures low molecular weight polystyrene-rich portions are formed. The number average molecular weight (M_n) is strongly reduced. P(S-b-EB-b-MMA) triblock copolymers show broadening of the MWD to higher and lower molecular weights at elevated temperatures, probably caused by chain scission and linking reactions of the EB block. M_n remains approximately constant. Up to 240°C the broadening of the MWD is not very pronounced. In comparison to unhydrogenated P(S-b-B-b-MMA) triblock copolymers, the thermal stability of P(S-b-EB-b-MMA) is greatly enhanced.

Introduction

Block copolymers containing a PMMA block receive increasing attention in the area of polymer blends (1,2). Especially P(S-b-MMA) block copolymers are frequently used as model system, because these polymers are readily accessible, PS and PMMA have nearly the same Tg and their physical properties are well-documented in literature (3,4). In the course of our work, we used P(S-b-MMA) diblock copolymers and P(S-b-EB-b-MMA) triblock copolymers as compatibilizers for polymer blends of poly(styrene-co-acrylonitrile) and poly(2,6-dimethyl-1,4-phenylene ether) (5-7). To prepare the blends close to equilibrium, they have to be annealed at temperatures as high as possible. Therefore it was important to investigate the thermal stability of these block copolymers under the conditions of sample preparation, i.e. melt pressing in vacuum. Investigation of the molecular weight distribution of narrow distributed samples is a sensitive tool to detect decomposition or crosslinking reactions and therefore a safe criterion to establish the limit of thermal stability.

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Experimental

Materials: The block copolymers were synthesized by sequential anionic polymerization in THF. P(S-b-EB-b-MMA) was prepared by hydrogenation of P(S-b-B-b-MMA) with tosylhydrazide. Details are given elsewhere (6,8). Table 1 gives the molecular characteristics of the P(S-b-MMA) diblock copolymer SM78 and the P(S-b-EB-b-MMA) triblock copolymer SEBM38 used in this study.

Table 1: Analytical results of block copolymers (see also ref.8)

BC	M_n^{GPC}	$M_n^{Osm.}$	M_w/M_n	w_{PS}	w_{EB}	w_{PMMA}
SM78	(136)	155	1.09	0.47	0	0.53
SEBM38	(189)	245	1.15	0.24	0.38	0.38

M_n^{GPC} = molecular weights of the block copolymers from GPC are too low, due to PS-calibration; $M_n^{Osm.}$= molecular weights from membrane osmometry; w_{PS}, w_{EB}, w_{PMMA} = weight fractions of the blocks determined from ^1H-NMR.

Thermal treatment: A vacuum hydraulic press with heatable plates was used to prepare samples of defined thermal history. 200mg of the pure block copolymers were heated in special molds at different temperatures for a defined time to give small discs (ϕ= 1,5cm). The cold filled molds were placed between the heated plates and the system was evacuated. The molding times were taken from placing the molds between the plates. The time the molds required to reach the temperature of the preheated plates is about 5-10min. Temperature was controlled by thermocouples in the heating plates to an accuracy of ± 2°C. After the specified molding times, the molds were quenched with water. Small pieces of the molded discs were dissolved in THF and investigated with GPC. In no case insoluble portions were formed.

GPC: GPC measurements were made with THF at a flow rate of 1ml/min on an apparatus equipped with a set of 10μm PL-Gel columns of pore size 10^5, 10^4, 10^3 and 10^2 Å. A refractive index and a UV (254nm) detector were used. Flow rates were corrected with toluene as internal standard. Calibration was done with PS-standards. Acquisition and analysis of data was done with a PC. Software allows to present the data scaled and flow-corrected.

Results and discussion

Assertion of the thermal stability of polymers largely depends on the conditions under which materials are testet (presence of oxygen, oxidative impurities, stabilizers etc.) and the criterions which are used to detect degradation (weight loss, alteration of chemical composition, spectroscopic changes etc.). In most cases, thermal degradation of polymers is accompanied by chain scission, cross linking and/or depolymerization (9). For polymers with narrow molecular weight distribution, GPC analysis is therefore a very sensitive tool to monitor degradation, because even minor changes will be reflected in a broadening of the molecular weight distribution. In the case of block copolymers, GPC analysis with two detection methods, which have different sensitivity for the blocks, gives information about changes in chemical composition with molecular weight.

The ceiling temperature of PMMA is 220°C (10). Therefore the PMMA block of P(S-b-MMA) and P(S-b-EB-b-MMA) block copolymers, can undergo depolymerization at temperatures above 220°C. Depending on the method of synthesis of PMMA, depolymerization is initiated at different temperatures. PMMA synthesized by radical polymerization is less stable, due to weak linkages in irregular structures from termination by disproportionation and recombination. In contrast to this, anionically prepared PMMA is much more stable because such weak linkages are not present (9,11-13).

Thermal stability of P(S-b-MMA)

The stability of P(S-b-MMA) was investigated using the high molecular weight block copolymer SM78 (see Table 1). In a first series of experiments, the sensitivity of the GPC method in detecting portions of PS-homopolymer in SM78 was testet. First the block copolymer SM78 was extracted with cyclohexane at 50°C (concentration < 1% w/v) to remove possible impurities of terminated homopolystyrene. About 1 wt% of homopolystyrene could be extracted. Small samples (25mg) of this "PS-free" material of SM78 were mixed with increasing amounts of the PS-precursor, which was isolated during the anionic synthesis of SM78. Figure 1 shows the GPC analysis of these mixtures with increasing amounts of PS precursor.

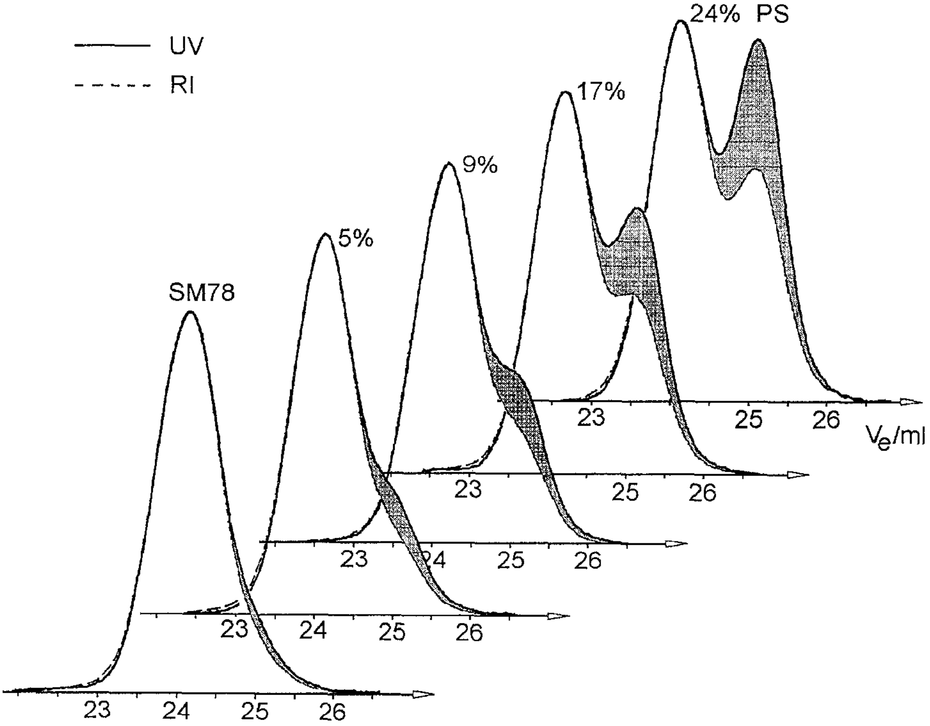

Figure 1: GPC analysis of mixtures of the P(S-b-MMA) block copolymer SM78 with increasing amounts (wt%) of PS-precursor; curves of RI- and UV-detection are normalized to the peak maximum of the block copolymer peak; shaded area: difference between UV- and RI-detection.

In contrast to PS, PMMA does not absorb at 254nm. Therefore homo-PS is detected much more sensitive by the UV-detection than the symmetric block copolymer SM78. In Figure 1 the peaks of the RI- and UV-detection were normalized to the peak maximum of the block copolymer peak. The shaded area corresponds to the difference between UV and RI-detection. The presence of PS precursor is obvious from the enhanced UV-detection on the low molecular weight side. In each mixture, RI- and UV-detection are identical on the high molecular weight side. In the pure block copolymer SM78 the signals of both detectors are identical, indicating that the chemical composition does not vary with molecular weight. Thus the comparison of RI- and UV-detection enables to recognize few percents of terminated PS-precursor. In general such a comparison of the UV- and RI-detection will give differences, if the ratio of PS:PMMA significantly changes with elution volume. These results show that less than about two percents of terminated homo-PS are present, if the traces of the RI- and UV-detection of P(S-b-MMA) are identical.

This procedure was also used to investigate the influence of thermal treatment on the molecular weight distribution of SM78. The samples were molded for 45min at different temperatures in vacuum. Figure 2 shows the changes in the molecular weight distribution of SM78 as the molding temperature is enhanced.

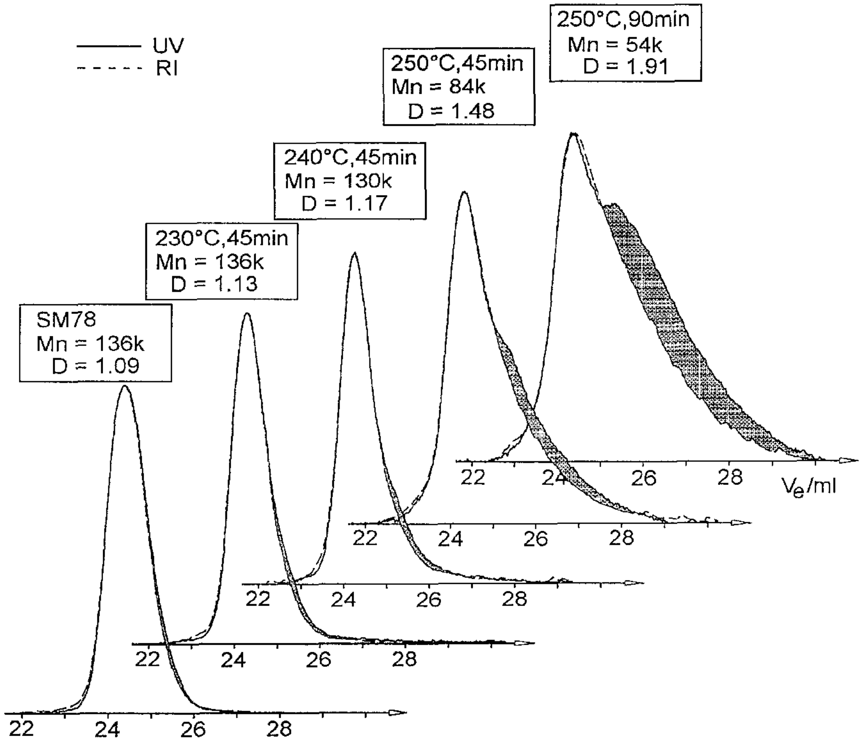

Figure 2: GPC analysis of the P(S-b-MMA) block copolymer SM78 molded at different temperatures; D = M_w/M_n; shaded area: difference between UV- and RI-detection.

Up to 240°C the molecular weight remains constant without broadening of the molecular weight distribution. At the temperature of 250°C, significant amounts of low molecular weight portions are formed and the overall molecular weight is strongly reduced. The low molecular weight portions show enhanced UV-absorption, indicating PS-rich material. Up to 250°C no changes occur on the high molecular weight side, i.e. no crosslinking or branching occurs. Most probably random scission of the PMMA block is associated with partial depolymerization. This explains the occurence of low molecular weight PS-rich portions. Nevertheless, at 250°C the rate of depolymerization of the PMMA block must still be low. The ^{1}H-NMR spectra of the sample which was molded at 250°C for 90min, did not show a reduced ratio of PMMA:PS according the integration of the ester methyl protons of PMMA versus the aromatic protons of PS. Moreover, the molded sheet showed no bubbles, as would be the case if excessive formation of volatile products occurs due to depolymerization.

Thermal stability of P(S-b-EB-b-MMA)

To enhance the thermal stability of P(S-b-B-b-MMA) triblock copolymers, the 1,2-polybutadiene midblock was hydrogenated with tosylhydrazide. Without hydrogenation the triblock copolymers with 1,2-PB readily crosslink. According to dynamic mechanical analysis excessive crosslinking occurs at temperatures above ≈150°C. Even triblock copolymers which were hydrogenated to 85 Mol% showed crosslinking in concentrated solution. Stabilizing agents could not prevent excessive crosslinking at molding temperatures above ≈200°C. The only possibility to prevent crosslinking at higher temperatures in the melt is the quantitative hydrogenation.

P(S-b-EB-b-MMA) triblock copolymers hydrogenated with tosylhydrazide contain about 3 Mol% tosyl groups incorporated in the EB-midblock. The stability of these materials was investigated using the triblock copolymer SEBM38 which contains 38 wt% EB-midblock (see table 1). The sample was reprecipitated two times from THF solution in methanol to remove residual p-toluenesulphinic acid, the main byproduct of the thermolysis of tosylhydrazide.

Figure 3 shows the GPC analysis of samples of the triblock copolymer SEBM38 molded at different temperatures. In contrast to the eluograms of the diblock copolymer SM78 (Fig.2), almost no differences between the RI- and UV-detections were observed. Therefore only the UV-detection curves are given in Figure 3. At molding temperatures above 200°C broadening of the molecular weight distribution to higher and lower molecular weights is observed. Even at 250°C no insoluble fractions are formed. At 250°C the polydispersity increased from 1.15 in the starting material to 1.56. Nevertheless, the number average molecular weight M_n shows almost no changes with increasing molding temperature. The narrow main block copolymer peak is preserved. Most of the material is unchanged. Obviously the effects of chain scission are balanced by linking reactions. The overall number of chains remains approximately constant. Thus in the temperature range between 200 and 250°C the degradation P(S-b-EB-b-MMA) proceeds by different pathways compared to P(S-b-MMA) diblock copolymers.

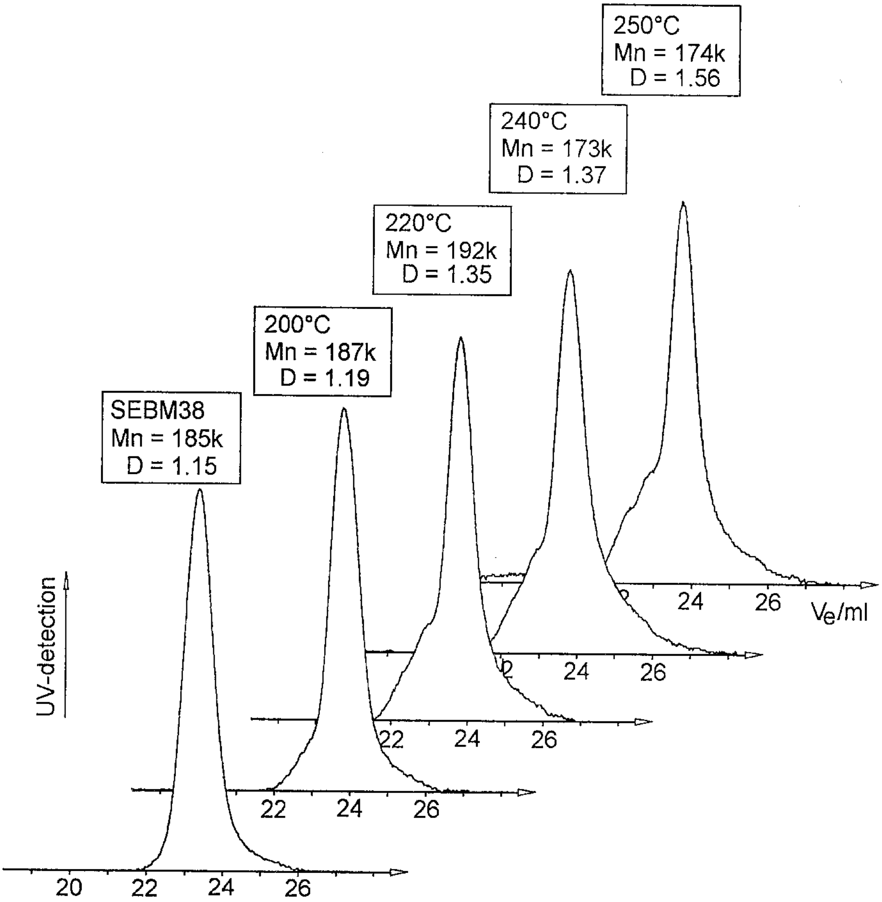

Figure 3: GPC analysis of the P(S-b-EB-b-MMA) triblock copolymer SEBM38 molded at different temperatures for 45min.

A possible explanation for the observed degradation behavior of SEBM38 is that the tertiary C-H bonds in the backbone of the EB block are involved in radical transfer reactions leading to a relative stable tertiary radical site in the backbone which can undergo fragmentation reactions, similar to the degradation of polypropylene (9). The scissioned EB chains can recombine or make a chain transfer. Such a scheme could explain why the number average molecular weight remains approximately constant, while the molecular weight distribution is broadened to both sides.

It has been also observed that traces of the strongly acidic p-toluenesulfinic acid favour the thermal degradation. Under identical conditions, less purified samples with residual sulphinic acid showed stronger broadening of the molecular weight distribution than carefully purified samples.

Conclusions

Up to 240°C P(S-b-MMA) diblock copolymers show no alterations of the molecular weight distribution under practical molding conditions in vacuum. At higher temperatures low molecular weight PS-rich portions are formed probably by random scission of the PMMA block. Up to 250°C no excessive depolymerization of PMMA is observed within 45min. In comparison with unhydrogenated or partially hydrogenated P(S-b-B-b-MMA) triblock copolymers, a strong improvement of the thermal stability is achieved in P(S-b-EB-b-MMA) triblock copolymers prepared by quantitative hydrogenation with tosylhydrazide. No insoluble portions are formed at temperatures up to 250°C. In the temperature range between 200°C and 240°C moderate broadening of the molecular weight distribution of P(S-b-EB-b-MMA) to higher and lower molecular weights is observed. The degradation behavior seems to be dominated by reactions of the EB midblock. The criterion of the broadening of the molecular weight distribution of initially narrow distributed block copolymers by thermal treatment is a very sensitive tool to detect degradation. With other criteria for example alteration of the chemical composition or formation of insoluble or volatile portions, the stability limit would be found much higher. Therefore the observed stability limit of ≈240°C is a very safe limit up to which these block copolymers or blends with these block copolymers can be molded in vacuum without degradation.

Acknowledgments

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