Thermal characterisation of Boc-aminostyrene/styrene copolymers latexes

V. L. Covolan[1], E. G. Fernandes, S. D'Antone, E. Chiellini[*]

Department of Chemistry and Industrial Chemistry, University of Pisa, via Risorgimento 35, 56126 Pisa, Italy

Abstract

Microspheres based on funcionalized polystyrene are used as supports for immunological reactions. New styrene/Boc-aminostyrene (St/BocAmSt) copolymers and the corresponding styrene–aminostyrene (St/AmSt) copolymers obtained as microspheres under dispersion polymerization conditions and successive deblocking reaction respectively, were characterized by thermogravimetry (TG) and differential scanning calorimetry (DSC). Thermal stability was found to be dependent on copolymer molecular weight and composition. The St/AmSt copolymers were more stable than St/BocAmSt copolymers and showed a direct relationship with AmSt content.

Glass transition temperature as a function of copolymer composition obeyed the Fox equation in good approximation. For low molecular weight copolymers the glass transition temperature was between 91°C [T_g poly(styrene)] and 151°C [T_g poly(Boc-aminostyrene). © 1999 Elsevier Science B.V. All rights reserved.

Keywords: DSC; TG; Polystyrene; Aminated styrene copolymers; Microspheres

1. Introduction

Latex microspheres obtained from modified polystyrene are efficient supports for immunological reactions [1]. Functional groups can be conveniently introduced on these microspheres susceptible to covalently bind antigens or antibodies [2–4]. Aminated polymeric microspheres permit direct diazotization on their surface. Consequently, they can react with immunoproteins in immunological assays. Typically, the aminated polystyrene microspheres can be produced in a sequence of different reaction stages consisting of: (i) preparation of polystyrene microspheres by emulsion polymerization; (ii) surfaces nitration of microspheres; (iii) reduction of nitrated microspheres [5]. The more direct way to obtain aminated polymeric microspheres by copolymerization of aminostyrene (AmSt) with styrene (St) was found not suitable due to the apparent low reactivity of AmSt [6]. A new synthetic procedure was adopted as based on the copolymerization of styrene with aminostyrene bearing the amino group protected with a blocking group easily removable by post polymer-analog reaction on the copolymer samples.

In the present work, we wish to report on the thermal property of the prepared polymers character-

---

*Corresponding author. Fax.: +39 050 28438

E-mail address: chlmeo@dcci.unipi.it (E. Chiellini)

[1]Present address: Physical-Chemisty Department of Chemistry Institute, Campinas University, UNICAMP, PO Box 6154, CEP 13083-970, Campinas SP, Brasil.

ization by DSC and TG of the styrene/aminostyrene copolymers obtained by polymerization performed both in solution and in dispersion.

2. Experimental

2.1. Materials

Styrene (Fluka) and aminostyrene (Aldrich Chemicals) monomers were distilled under vacuum prior to polymerization. α,α'-azobisisobutyronitrile (AIBN) (Fluka) initiator was recrystallised from ethyl alcohol (Carlo Erba). Di-tert-butyl dicarbonate [(Boc)$_2$O] (Aldrich Chemicals) was used as received. Poly(vinylpyrrolidone) (Fluka) having $\bar{M}_w$ 360.000 was used as emulsifier. Isopropyl alcohol and deionised water were used as received. Toluene was distilled under vacuum prior to use.

2.2. Synthesis

Copolymer samples used in this work were obtained from by solution and dispersion polymerization. A detailed description of the two procedures is reported in a forthcoming paper [7].

Prior to thermal analysis investigation, the purified microspheres obtained from dispersion polymerization were solubilised in chloroform followed by precipitation in n-hexane and finally dried under vacuum for 24 h.

The copolymer samples obtained by polymerization in solution were reprecipitated with methanol from solution in toluene.

2.3. Thermal analysis

Investigations by differential scanning calorimetry (DSC) and thermogravimetry (TG) were performed on a Mettler TA 4000 System. A TG50/M3 thermobalance was used for TG measurements. Samples of about 10 mg were scanned at 10°C min^{-1} from 25°C to 700°C under nitrogen atmosphere with a flow rate of 200 ml min^{-1}. A DSC 30 cell was used for the investigation of the thermodynamic properties of the polymeric materials. Samples of 4–6 mg were heated, cooled and re-heated at 10°C min^{-1} from 0°C to 200 °C under a 20 ml min^{-1} nitrogen flow.

3. Results and discussion

Molecular characteristics of styrene/Boc-aminostyrene copolymers (St/BocAmSt) obtained from solution and dispersion polymerization are shown in Tables 1 and 2, respectively.

Tables 3 and 4 show pyrolysis data of St and BocAmSt polymers and their copolymers synthesised by solution polymerization. BocAmSt polymer decompose in nitrogen atmosphere with three distinct steps of weight loss leaving about 6 wt% of residue at 520°C. On the other hand, polystyrene tend to depolymerize only in one step corresponding to a temperature range comprised in the third step recorded for BocAmSt polymer. First and second steps recorded in St/BocAm are associated with BocAmSt and, by mass balance, the first step can be attributed to methane evolution. Consequently, the ratio between second and first steps will be constant with a value of ca. 3.3 (Table 3). However, the copolymer with about 75 wt%

Table 1

Molecular characteristics of St/BocAmSt copolymers obtained from solution polymerization

St feed[a] (wt%)	Conv. (wt%)	$\bar{M}_w$	$\bar{M}_n$	ID[b]	St copol.[c] (wt%)	St copol.[d] (wt%)
0.0	83	7400	4100	1.8	0.0	0.0
33.4	71	8100	3900	2.0	31.1	23.2
52.3	55	6000	3600	1.6	44.5	35.9
80.2	44	5700	3800	1.5	75.4	61.1
100	42	22 038	14 773	1.5	100.0	100.0

[a] Styrene (St) weight fraction in reaction feed of St/BocAmSt copolymerization.
[b] ID = Polydispersity.
[c] Styrene (St) weight fraction in St/BocAmSt copolymer determined by NMR.
[d] Styrene (St) weight fraction in St/BocAmSt copolymer as determined by TG.

Table 2
Molecular characteristics of St/BocAmSt copolymers obtained from dispersion polymerization

St feed[a] (wt%)	Conv. (wt%)	$\bar{M}_w$	$\bar{M}_n$	ID[b]	St copol.[c] (wt%)	St copol.[d] (wt%)
32.2	89	22 800	11 400	2.0	31.3	34.4
52.7	87	45 800	29 100	1.6	51.3	50.7
64.9	88	67 600	35 650	1.9	64.8	64.6
80.9	91	51 000	24 400	2.0	77.9	74.6
89.6	93	46 100	24 600	1.9	87.8	84.0
97.7	98	10 200	5160	1.9	94.7	–

[a] Styrene (St) weight fraction in reaction feed of St/BocAmSt copolymerization.
[b] ID = Polydispersity.
[c] Styrene (St) weight fraction in St/BocAmSt copolymer devtermined by NMR.
[d] Styrene (St) weight fraction in St/BocAmSt copolymer as determined by TG.

Table 3
Weight loss decomposition steps of St/BocAmSt copolymers from solution polymerization

St cont.[a] (wt%)	1st step (wt%)	2nd step (wt%)	3rd step (wt%)	Step ratio Wt_2/Wt_1	Step ratio Wt_3/Wt_2	Residue[b] (wt%)
0.0	11.40	38.25	45.08	3.35	1.18	5.83
31.1	8.58	29.57	58.12	3.45	1.96	3.04
44.5	6.72	24.08	64.32	3.58	2.67	3.49
75.4	7.18	14.69	78.42	2.05	5.34	1.09
100.0	–	–	100.00	–	–	0.00

[a] Styrene (St) content in St/BocAmSt copolymer as determined from NMR.
[b] Residue at 520°C.

Table 4
Thermal decomposition temperatures of St/BocAmSt copolymers from solution polymerization[a]

St cont.[b] (wt%)	T_1 (°C)	T_{p-1} (°C)	T_2 (°C)	T_{p-2} (°C)	T_3 (°C)	T_{p-3} (°C)
0	83.3	119.5	194.0	209.3	351.7	386.7
31.1	64.7	103.5	198.9	214.8	351.9	382.0
44.5	89.5	110.3	194.0	214.0	357.7	386.7
75.4	72.7	93.8	196.9	221.0	359.4	389.0
100	–	–	–	–	360.1	389.0

[a] T_i onset decomposition temperature of each step; T_{p-i} maximum temperature of the first derivative curve.
[b] Styrene (St) content in St/BocAmSt copolymer as determined from NMR.

of St showed a lower value. A possible explanation would be the presence of residual traces of solvent that evaporate within the same temperature range of the first step of weight loss.

Third step of weight loss in copolymers samples corresponds to the depolymerization of styrene and aminostyrene monomeric units. So, assuming that the decomposition of the BocAmSt in the copolymer has the same mechanism as that of the homopolymer, the ratio between the weight loss recorded in the third and second steps will permit to estimate styrene content in the copolymer as indicated by the following relationships:

$$\frac{(Wt_3)}{Wt_2} = \frac{(Wt_3)_{St}}{Wt_2} + \frac{(Wt_3)_{Boc}}{Wt_2}, \tag{1}$$

$$\frac{(Wt_3)_{Boc}}{Wt_2} = \text{constant}, \tag{2}$$

$$(Wt_3)_{Boc} = \text{constant} \cdot Wt_2, \tag{3}$$
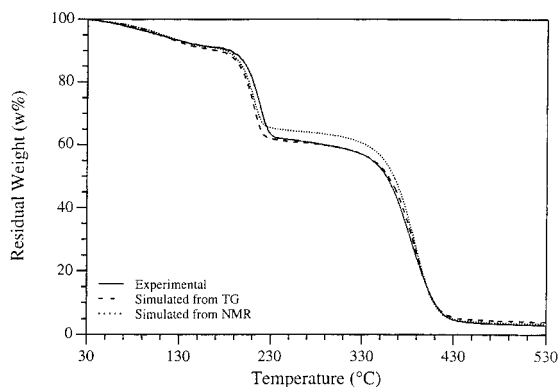
$$(Wt_3)_{St} = Wt_3 - (Wt_3)_{Boc}, \tag{4}$$

Fig. 1. Experimental and simulated TG traces of St/BocAmSt copolymer (33.4/66.6 feed wt% — Table 1) obtained from solution polymerization. Simulated St/BocAmSt composition are 23.2/76.8 wt% from TG data and 31.1/68.9 wt% from NMR data.
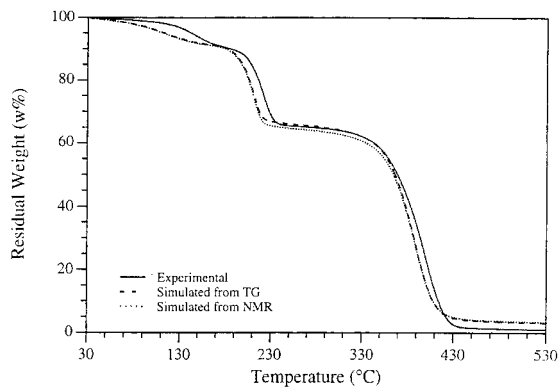

Fig. 2. Experimental and simulated TG traces of St/BocAmSt copolymer (32.2/67.8 feed wt% — Table 2) obtained from dispersion polymerization. Simulated St/BocAmSt composition are 34.4/65.6 wt% from TG data and 31.3/68.7 wt% from NMR data.

where Wt_3 is the weight loss in the third step from copolymer; $(Wt_3)_{St}$ and $(Wt_3)_{Boc}$ represent the weight losses of styrene recorded in the third step from both styrene and BocAmSt segments, respectively; and Wt_2 represents the weight loss recorded in the second step corresponding to BocAmSt.

By taking for the "constant" the value of 1.18 as obtained from BocAmSt homopolymer (Table 3), it is possible to calculate styrene content in the copolymer. The content obtained from TG data is lower than that estimated from NMR. The differences is about 20% with respect to the composition evaluated from NMR and decreases when St content increases. BocAmSt was found to be more reactive than styrene [6].

By assuming that copolymer decomposition obeys an additivity rule, the simulated and experimental TG traces were compared. Fig. 1 shows simulate traces from NMR and TG copolymer composition data. The better overlapping was observed for simulations with copolymer compositions from TG; exception was verified for St/BocAmSt at a composition 36/64 by weight where the second step of simulated trace is slightly higher than the experimental one. This means that in the analyzed copolymer sample the content of styrene monomeric units is higher than the value expected from the additive principle. Besides, second step does begin at a temperature higher than that of simulated one. This change on reaction kinetic can be an evidence that copolymers are more stable than corresponding homopolymers. Furthermore, the data

suggest that there is a composition dependence of reaction kinetics, especially in the second step, as indicated by the temperature of the maximum rate of weight loss (T_{p-i}) (Table 4).

The first and second onset decomposition temperatures (T_1 and T_2) did not show a systematic dependence on the composition. On the other hand, the onset temperature of the third step (T_3) increases with increasing content of the more stable styrene comonomer from 352°C (BocAmSt) to 360°C (St).

For the copolymer samples obtained in dispersion, the compositions of copolymers estimated by NMR and TG (Fig. 2 and Table 2), displayed a better correlation than that recorded for the solution copolymers. Dispersion copolymers were obtained at a higher conversion rate than those prepared in solution. Consequently, copolymer composition was closer to that of the monomeric feed.

Weight loss from decomposition of St/BocAmSt copolymers obtained by dispersion polymerization are reported in Table 5. The weight loss ratio between the second and third step is lower than that presented by the homopolymer BocAmSt (Table 3) and decreases when styrene content increases. Residual traces of solvents could be claimed as responsible for that behavior. By calculating approximately the amount of residual solvent in the samples Eqs. (5)–(7), it was verified that there is a direct relationship with molecular weight of copolymers. Although these samples were dried under reduced pressure for about 24 h, the

Table 5
Weight loss decomposition steps of St/BocAmSt copolymers from dispersion polymerization

St cont.[a] (wt%)	1st step (wt%)	2nd step (wt%)	3rd step (wt%)	Step ratio (Wt$_2$/Wt$_1$)	Step ratio Wt$_3$/Wt$_2$	Residue[b] (wt%)
31.3 (BOC)	9.51	25.56	63.84	2.69	2.50	1.09
51.3 (BOC)	9.07	18.19	71.61	2.00	3.94	1.13
64.8 (BOC)	9.39	11.93	78.55	1.27	6.58	0.13
77.9 (BOC)	7.41	8.27	84.32	1.12	10.20	nd
87.8 (BOC)	5.97	4.59	89.44	0.77	19.49	nd
94.7 (BOC)	4.39	nd[c]	95.36	–	–	0.25
51.3 (NH$_3^+$)	3.02	6.29	89.02	2.08	14.15	1.67
64.8 (NH$_3^+$)	7.84	2.36	87.62	0.30	37.13	2.18
77.9 (NH$_3^+$)	4.32	4.28	89.05	0.99	20.81	2.35
87.8 (NH$_3^+$)	nd	2.14	97.12	–	–	0.74
94.7 (NH$_3^+$)	nd	nd	99.14	–	–	0.86
51.3 (NH$_2$)	nd	2.39	94.73	–	39.64	2.88
64.8 (NH$_2$)	nd	nd	98.47	–	–	1.53
77.9 (NH$_2$)	nd	nd	99.26	–	–	0.74
87.8 (NH$_2$)	nd	1.93	97.38	–	50.46	0.69
94.7 (NH$_2$)	nd	nd	99.31	–	–	0.69

[a] Styrene (St) content in St/BocAmSt copolymer as determined from NMR.
[b] Residue at 520°C.
[c] Not detected.

treatment was not apparently as efficient as expected especially for higher molecular weight copolymers.

$$Wt_{1'} = Wt_{sol} + Wt_{1St}, \tag{5}$$

$$\frac{Wt_2}{Wt_1} \approx 3.3, \tag{6}$$

$$Wt_{sol} = Wt_{1'} - \frac{Wt_2}{3.3}, \tag{7}$$

where $Wt_{1'}$ is the weight loss observed in the first decomposition step of St/BocAmSt and residual solvent, and Wt_2 the weight loss observed in the second step.

Some samples of deprotected styrene–ammonium copolymers $\left[St/St\left(NH_3^+\right) \right]$ and styrene/aminostyrene $[St/St(NH_2)]$ presented a first and/or a second weight loss step that were characteristic of BocAmSt segments. It was noticed above that these samples did not retain a microsphere shape after the submission. Hence, as the reactions for amine deprotection were occurring at surface level some BocAmSt segments migrating from microsphere bulk was assumed to be present.

Copolymers from dispersion polymerization were slightly more stable than the samples attained from solution polymerization (Tables 4 and 6) and opposite

behavior of T_3 was verified between them. This would mean that, copolymers from dispersion polymerization, with lower styrene content, were more stable than those with higher styrene content as happened with copolymers from solution polymerization. For example, T_3 changed from 362°C for the sample containing 31.3 wt%-St to 358°C for the sample containing 77.9 wt%-St in dispersion copolymer while corresponding values detected for the copolymers prepared in solution were 352°C for a sample containing 31.1 wt%-St and 359°C for 75.4 wt%-St. However, it can be observed that T_3 recorded on dispersion copolymers has a direct correlation with the molecular weight (Table 2).

3.1. Glass transition temperature

Glass transition temperatures measured on the second heating scan are collected in Table 7 and Fig. 3 for both series of copolymers obtained by copolymerization in solution and dispersion. All samples exhibited a single T_g as in the case of the corresponding homopolymers. Copolymers from solution polymerization have lower T_g than those from dispersion polymerization. This behavior can be attributed to the difference in molecular weight within the two series of copoly-

Table 6
Thermal decomposition temperatures of St/BocAmSt copolymers from dispersion polymerization [a]

St cont.[b] (wt%)	T_1 (°C)	T_{p-1} (°C)	T_2 (°C)	T_{p-2} (°C)	T_3 (°C)	T_{p-3} (°C)
31.3 (BOC)	122.4	146.8	204.5	220.5	362.3	399.0
51.3 (BOC)	119.8	141.2	206.1	223.3	358.5	396.2
64.8 (BOC)	93.9	118.5	206.5	229.0	364.6	396.2
77.9 (BOC)	104.5	121.3	209.5	229.0	358.2	390.5
87.8 (BOC)	99.7	115.7	214.7	231.8	357.1	387.7
94.7 (BOC)	93.3	107.2	–	–	354.8	387.7
51.3 (NH_3^+)	64.5	75.1	249.7	265.8	370.5	393.3
64.8 (NH_3^+)	101.6	121.3	224.6	243.2	367.9	393.3
77.9 (NH_3^+)	81.6	98.7	219.6	243.2	367.9	393.3
87.8 (NH_3^+)	–	–	158.8	199.2	357.1	387.7
94.7 (NH_3^+)	–	–	–	–	357.1	387.7
51.3 (NH_2)	–	–	247.3	268.7	370.0	393.3
64.8 (NH_2)	–	–	–	–	362.5	390.5
77.9 (NH_2)	–	–	–	–	358.1	387.7
87.8 (NH_2)	–	–	192.1	206.0	355.8	384.8
94.7 (NH_2)	–	–	–	–	357.7	387.7

[a] T_i onset decomposition temperature of each step; T_{p-i} maximum temperature of the first derivative curve of each step.
[b] Styrene (St) content in St/BocAmSt copolymer as determined from NMR.

Table 7
Glass transition temperatures of the polymers from dispersion and solution polymerizations

St sol.[a] (wt%)	T_g (°C)	St disp.[b] (wt%)	T_g^c (°C)	T_g^d (°C)
0.0	150.8	–	–	–
31.1	130.0	31.3	145.8	–
44.5	120.0	51.3	131.6	124.1
–	–	64.8	118.3	113.3
75.4	93.3	77.9	113.3	109.1
–	–	87.8	108.3	106.7
–	–	94.7	104.2	103.2
100.0	91.3	–	–	–

[a] Styrene (St) weight fraction from NMR of solution copolymers.
[b] Styrene (St) weight fraction from NMR of dispersion copolymers.
[c] Values relevant to the bocked copolymer samples.
[d] Values relevants to the corresponding debocked samples.

mers. However, the behavior as a function of styrene content is more or less parallel. Poly(BocAmSt) has a T_g ca. 60°C higher than that of poly(styrene) (PSt) due to the restriction in conformational freedom played by the Boc moiety. PSt obtained by solution polymerization with $\bar{M}_n$ of 14 770 has a T_g of 91.3°C that is about 5°C higher than that obtained by ESR data of Kumler et al. [8] for equivalent molecular weight. By considering that $\bar{M}_n$ by copolymers obtained by dispersion copolymerization is about 28 000, it can be reasonably supposed that T_g relevant to PSt homopolymer should

be 94°C [8]. Linear extrapolation (correlation coefficient = 0.991) of experimental T_g data observed for dispersion St/BocAmSt copolymers gave a T_g value of 164.7°C for BocAmSt homopolymer and 99.3°C for St homopolymer. This last one is practically coincident with the value reported by Kumler.

Glass transition temperatures of StAmSt copolymers (T_g (NH_2)) are lower than the values observed for the relevant precursors St/BocAmSt copolymers. The difference between them is smaller at lower styrene contents in the copolymer.
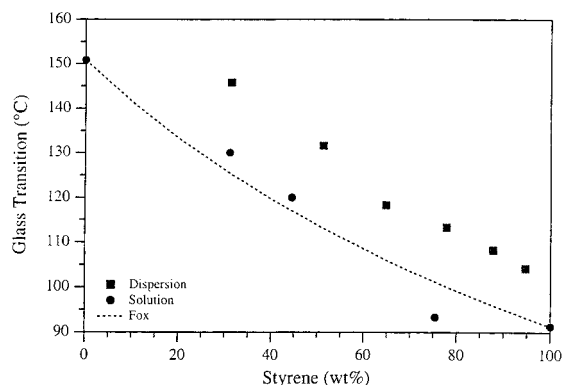
Fig. 3. Glass transition temperature (T_g) as a function of styrene content in St/BocAmSt copolymers from solution and dispersion polymerization.

Prediction of the glass transition temperatures according to Fox [9], as a function of the copolymer composition for samples of the solution series (Fig. 3, dashed line), indicates the presence of a slight positive deviation until approximately 50 wt%-St. On the other hand, at a styrene content of 78 wt% a negative deviation from Fox trace was observed.

4. Conclusions

Thermogravimetric analysis of styrene/Boc-aminostyrene copolymers (PSt/BocAmSt) allowed to determine the effect of copolymer compositions and polymerization conditions on their thermal stabilities. Copolymers from solution polymerization were less stable than those obtained by dispersion polymerization probably due to their lower molecular weight. However, all the experimental findings indicated that copolymers were more stable than the expectations from the additive principle.

A single T_g was detected for copolymers with values included between those of the parent homopolymers. The introduction of Boc group on aminostyrene homopolymer increased T_g of about 60°C. Glass transition temperatures as a function of the copolymer composition from solution polymerization could be predicted by Fox equation for styrene contents up to 50 wt%.

Acknowledgements

References

[1] S. Slomkowski, D. Kowalczyk, M. Trznadel, TRIP 3 (1995) 297–304.

[2] J.H. Braybrook, L.D. Hall, Prog. Polym. Sci. 15 (1990) 715–734.

[3] W.H. Scouten, Immobilized enzymes, in: Solid Phase Biochemistry, Wiley, 1983, pp. 253–392.

[4] A. Rembaum, S.P.S. Yen, R.S.J. Molday, Macromol. Sci. Chem. A 13(5) (1979) 603–632.

[5] V.L. Covolan, L.H.I. Mei, C.L. Rossi, Polymers for Advanced Technologies 8(1) (1996) 44–50.

[6] V.L. Covolan, Preparação de microesferas poliestirênicas aminadas através de copolimerização entre estireno e aminoestireno para utilização em testes imunológicos, Ph.D. Thesis, Universidade Estadual de Campinas, UNICAMP, Brasil, 1998.

[7] V.L. Covolan, G. Ruggeri, S. D'Antone, E. Chiellini, submitted.

[8] P.L. Kumler, S.E. Keinath, R.F. Boyer, J. Macromol. Sci. Phys. B 13 (1977) 631.

[9] Edith A. Turi (Ed.), Thermal Characterization of Polymeric Materials, vol. 1, 2nd ed., Academic Press, San Diego, 1997.