Styrene–*tert*-Butyl Methacrylate and Styrene–Methacrylic Acid Block Copolymers: Synthesis and Characterization

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ABSTRACT: Sequential living anionic polymerization techniques were used for synthesis of block copolymers of styrene and *tert*-butyl methacrylate. Cumylpotassium and naphthalene–potassium complexes served as initiators for diblock and triblock copolymers, respectively. The synthetic procedure and apparatus are described in detail. The copolymers as well as their polystyrene blocks had unimodal distribution of molecular weights. Their polydispersity $\bar{M}_w/\bar{M}_n$ was typically less than 1.1. Procedures were also developed for fluorescence labeling of the copolymers at the methacrylate end of the molecule by dansyl or anthryl moieties and at the beginning or end of the polystyrene block by naphthyl moieties. In the next synthetic step, the *tert*-butyl ester groups were hydrolyzed off, leaving block copolymers of styrene and methacrylic acid. The copolymers were characterized by gel permeation chromatography, light scattering, viscometry, proton NMR, thermogravimetric analysis, and differential scanning calorimetry.

In our broader research project, we are concerned with special properties of block copolymers and, especially, of hydrophobic/hydrophilic block copolymers. These copolymers exhibit interesting domain structures in the solid state and form spherical micelles in selective solvents.[1–3] For the hydrophobic/hydrophilic block copolymers this selective solvent can be water or aqueous buffers allowing for formation of micelles having hydrophobic cores.[1,3] In this paper we report the synthesis of one class of these copolymers: diblock and triblock copolymers of styrene and methacrylic acid. In order to facilitate the studies of the domains and micelles, we have also incorporated fluorescent probes into some polymer samples: naphthyl moiety into the hydrophobic part and dansyl or anthryl moiety into the hydrophilic part. Some molecular characteristics of our copolymers are also reported.

Anionic polymerization is the synthetic procedure of choice for preparation of block copolymers with controlled architecture and narrow distribution of molecular weights. Methacrylic acid cannot be polymerized anionically; we have therefore used its *tert*-butyl ester instead and removed the *tert*-butyl group by hydrolysis. While our procedure consists of steps that were reported by a number of investigators,[4–10] a rather rigid synthetic protocol has to be adhered to when copolymers of predetermined architecture and block sizes are to be obtained. We consider it therefore worthwhile to describe our procedure in some detail.

We have chosen tetrahydrofuran (THF) as the solvent for polymerization, and as initiators, cumylpotassium for the diblock copolymers and potassium–naphthalene complex for the triblock ones. Originally, the anionic polymerizations were performed in high vacuum with utilization of break-seal techniques.[11–13] While the procedure yielded well-defined polymers, it was cumbersome and required a long preparation for each experiment. It was reported recently[5,14] that polymerization performed in an inert atmosphere led to equally good polymers. We have therefore designed an apparatus consisting of a high-vacuum line into which it was possible to admit highly purified nitrogen. All the connections were through joints allowing fast assembly and disassembly of the apparatus.

Our synthetic sequence consisted of addition of a calculated amount of the initiator to THF and fast addition of styrene. The synthesis of the methacrylate blocks must be done very carefully; the methacrylate ester group could be attacked by carboanions in an unwanted side reaction.[10,15–18] The styryl anion is too energetic; before the methacrylate monomer is added it is necessary to reduce the activity of the growing chain by addition of 1,1-diphenylethylene (DPE). This monomer does not polymerize; consequently, only one molecule of DPE is incorporated into each growing chain.[19] The ester groups may be attacked also by the growing methacrylyl anions. This reaction is prevented by a careful slow polymerization during which the temperature is not allowed to exceed −78 °C. Finally, the polymerization was terminated by methanol.

Labeling by naphthyl moieties was achieved by addition of 2-vinylnaphthalene: it was added either at the beginning of the polymerization for labeling at the polystyrene end of the copolymer (or in the middle of polystyrene chain in the case of the triblocks) or before the addition of DPE for labeling at the block boundary. The reactivity of 2-vinylnaphthalene is similar to that of styrene, and the two monomers may be sequenced at will. Labeling by the dansyl and anthryl groups was achieved by terminating the chain by dansyl chloride or (chloromethyl)anthracene, respectively. When a substoichiometric amount of the labeling agent was added, the resulting sample consisted of labeled and unlabeled molecules that had otherwise identical architecture. Such samples are required for some studies of fluorescent behavior. We have also prepared samples that carried both the naphthalene and the dansyl label.

Experimental Section

The high-vacuum line was constructed in a routine way and a vacuum of 5×10^{-6} Torr was routinely achieved. It was possible to isolate part of the evacuated space (including the reactor) and fill it with nitrogen having a positive excess pressure. The nitrogen stream (all copper or glass tubing) was dried first by a slurry of sodium and paraffin oil and then by a molecular sieve; the last traces of oxygen were absorbed on a column of silica gel impregnated by manganous oxide (MnO) which is an efficient scavenger of oxygen.

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The reactor was a 1-L round-bottom flask with six necks. The necks had standard joints with Rodavis screw threads that are used without grease. The central neck was connected to the high-vacuum line by a connecting tube with a high-vacuum Teflon stopcock and an ACE threaded joint equipped with a Teflon O ring. A capillary leading through the middle of the connecting tube allowed for withdrawal of a sample from the reactor when needed. Graduated ampoules filled with individual reaction ingredients were attached to the side necks of the reactor and tightly closed with screw caps.

Before the individual ingredients were transferred into the ampoules, they had to be carefully purified and dried: even the tiniest traces of water or other impurities can ruin anionic polymerization. All of the glassware was cleaned and kept in the oven at 130 °C for at least 24 h. Before filling, the ampoules were evacuated, flame heated, and cooled in the vacuum line. The ampoules were used for monomer 1 (styrene), monomer 2 (*tert*-butyl methacrylate), initiator, DPE, and methanol (used for termination). Whenever a sixth ampoule with a labeling compound (vinylnaphthalene, dansyl chloride, or (chloromethyl)anthracene) was needed, one of the necks was furnished with a Y-piece and two ampoules were attached to it.

Styrene (Aldrich) was freed from the inhibitor, dried by stirring with calcium hydride for 4 h, and distilled into a predried and flame-heated container. It was further treated with dibutylmagnesium for about 3 h and then distilled into the ampoule, which was subsequently filled with purified dry nitrogen.

tert-Butyl methacrylate (courtesy of Rohm Tech) was also freed from the inhibitor and treated with calcium hydride for 4 h. After distillation, it was treated with a mixture of triethylaluminum and diisobutylaluminum hydride[6,7] that deactivated the remaining traces of *tert*-butyl alcohol, passed through a column of activated neutral alumina, and distilled into the ampoule.

1,1-Diphenylethylene (Aldrich) was purified by distillation from *sec*-butyllithium in vacuum. Then, THF was distilled into the same ampoule in order to dilute DPE to the required concentration. A tiny amount of *sec*-butyllithium was added to the ampoule. It produced the slightest pink tinge that certified that no quenching impurity was present in the ampoule. (Quenching some growing chains between the addition of both monomers would be most unfortunate; it would contaminate the copolymer by homopolystyrene.)

2-Vinylnaphthalene, dansyl chloride, and (chloromethyl)anthracene, which are solid, were dissolved, respectively, in a minimum amount of dry THF and transferred by syringe into dry ampoules. Additional THF was then distilled into the ampoules to dilute them to the required concentration.

Methanol was degassed and distilled directly into the ampoule.

Cumylpotassium was prepared by reacting methyl phenylisopropyl ether (MPIPE) with potassium metal[20] at room temperature in THF.

Potassium–naphthalene complex was also prepared in THF solution by reacting naphthalene with potassium metal. The initiator solutions were then filtered through a glass frit directly into their respective ampoules. Their concentrations were obtained by titrating acetanilide with the initiator solution. Acetanilide (Aldrich) was recrystallized from toluene and stored in a desiccator.

MPIPE was prepared from α-methylstyrene using a published procedure[20]; it was fractionated using 30-in. column at 20 Torr. Its purity was checked by gas chromatography.

Tetrahydrofuran (THF) was stirred with calcium hydride for a couple of days, distilled, treated with sodium dispersion in the presence of naphthalene for 24 h, and distilled again into a storage container coated with sodium mirror and holding some sodium naphthalene complex.

Polymerization Reaction. The assembled reactor was connected to the high-vacuum line, evacuated, flame heated, and cooled. Then it was purged three times with purified dry nitrogen and evacuated each time. About 400 mL of THF was distilled from the storage container directly into the reactor that was cooled to −78 °C by a dry ice/2-propanol bath. The reactor was filled with nitrogen and closed by a stopcock. The solvent was titrated with the initiator solution to eliminate all reactive impurities, the calculated amount of the initiator was added, and the reactor was cooled back to low temperature. The reactor contents were stirred continuously by a magnetic stirrer. The entire amount of styrene was then added quickly all at once, and the reaction was allowed to proceed to completion for about 10 min. Then about 30 mL of the solution was siphoned into a receiver flask attached to the reactor assembly and deactivated by methanol. The resulting polystyrene sample was used later for estimating the molecular weight of the polystyrene block by GPC. Then the solution of DPE was added to the reactor (twice the amount needed for capping the styryl anions). The second monomer (*t*BMA) was then added drop by drop at a very low rate. After the addition was completed, the reaction was allowed to proceed for another 0.5 h and then was terminated by degassed methanol. The reaction assembly was dismantled, and the copolymer was precipitated by adding the solution to a large amount of mixture of methanol and water, filtered, and dried.

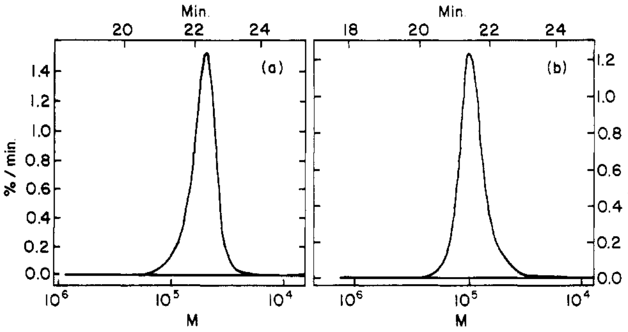

Figure 1. GPS elution profiles for (a) the central polystyrene block of the copolymer BSB-4 and (b) the copolymer BSB-4.

The hydrolysis of tBMA blocks in the copolymers was accomplished using aqueous hydrochloric acid in 1,4-dioxane at 85 °C for about 5 h. After the hydrolysis, the solution was dried by anhydrous sodium sulfate, filtered, and precipitated into excess cold hexane. The product was redissolved in dioxane and freeze-dried. Copolymers containing a larger molar fraction of styrene can also be hydrolyzed in wet toluene using catalytic amount of *p*-toluenesulfonic acid at 80 °C for 4 h. The resulting product was precipitated into excess cold hexane, filtered, dried, redissolved in dioxane, and freeze-dried.

Gel permeation chromatography (GPC) experiments were performed using a Spectra-Physics GPC instrument, with an Iso-Chrome LC Pump, an SP4270 Integrator, and Spectra-Physics GPC/PC Software. Three 10-μm particle size 25-cm × 8-mm Phenogel columns from Phenomenex (one column 100A, two-columns 0–10 000K mixed bed) were used as the stationary phase; THF at 25 °C was the mobile phase. As a detector we have used a Spectra-Physics variable wavelength UV–visible detector (operated at 254 nm). The calibration was based on polystyrene standards obtained from Pressure Chemicals and on cubic type regression. Typical GPC elution profiles for polystyrene block and for the corresponding block copolymer are presented in Figure 1.

Intrinsic viscosities in THF were determined using an Ubbelohde viscometer with photoelectric registration of flow times at 25 ± 0.01 °C.

Proton NMR spectra were measured by General Electric QE300 MHz NMR spectrophotometer.

Thermogravimetric and differential scanning calorimetric analyses (TGA and DSC) were performed using a Perkin-Elmer analysis system DSC7 equipped with thermal analysis data station.

Static light scattering was measured using a Sofica instrument equipped with a He–Ne laser. The data were treated by the standard Zimm method.

Results and Discussion

We have prepared a significant number of block copolymer samples. We have designated them by symbols composed of letters signifying the sequence of blocks and labels from one end of the chain to the other. In these symbols, S stands for polystyrene blocks, A for poly(methacrylic acid) block, B for poly(*tert*-butyl methacrylate) block, N for 2-vinylnaphthalene label, D for dansyl

Table I
Molecular Weights, Polydispersities, Compositions, and Intrinsic Viscosities of Diblock Unhydrolyzed Copolymers and Apparent Degrees of Hydrolysis of Hydrolyzed Copolymers Prepared from Them

sample[a]	$\bar{M}_{w,GPC} \times 10^{-3}$	$\bar{M}_{w,s} \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	mol % PS NMR	mol % PS GPC	$[\eta]_{THF}^{25}$	x_{hydr}, %	sample[b]
SB-1	50.4	24.4	1.09	56	56	22.0	100	SA-1
SB-2	84.8	24.4	1.15	36	36	33.7	99	SA-2
SB-3	138.7	24.4	1.19	24	23	49.7	97	SA-3
SB-4	34.3	24.8	1.06	80	78	20.6	104	SA-4
SB-5	44.0	27.8	1.05	73	70	24.7	99	SA-5
SB-6	17.1	6.7	1.16	60	47	11.9	98	SA-6
SB-7	150.4	95.7	1.05	70	70	69.6	100	SA-7
SB-8	200.1	134.0	1.06	70	74	75.0	97	SA-8
SB-9	25.4	10.8	1.07	53	50	16.6		SA-9
SB-10	57.8	30.1	1.10	60	60	31.7		SA-10
N4SB-2	60.4	21.3	1.08	45	43	26.1	96	N4SA-2
N1SB-3	100.6	38.8	1.07	46	47	42.0	99	N1SA-3
N1SB-4	67.2	34.0	1.07	59	58		99	N1SA-4
SBD-1	52.3	24.5	1.10	54	54		101	SAD-1
N1SBD-1	61.2	26.2	1.15	51	51		99	N1SAD-1
SN1B-1	54.4	22.8	1.15	48	50		101	SN1A-1
SN1BD-1	57.0	22.8	1.17	47	48		100	SN1AD-1
N1SBAn-1	90.0	35.2	1.07	45	47		102	N1SAAn-1
SN1BAn-1	79.6	31.4	1.09	46	47		102	SN1AAn-1

[a] Before hydrolysis. [b] After hydrolysis.

Table II
Molecular Weights, Polydispersities, Compositions, and Intrinsic Viscosities of Triblock Unhydrolyzed Copolymers and Apparent Degrees of Hydrolysis of Hydrolyzed Copolymers Prepared from Them

sample[a]	$\bar{M}_{w,GPC} \times 10^{-3}$	$\bar{M}_{w,s} \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	mol % PS NMR	mol % PS GPC	$[\eta]_{THF}^{25}$	x_{hydr}, %	sample[b]
BSB-3	81.4	45.0	1.09	61	63	36.3	93	ASA-3
BSB-4	97.6	55.9	1.09	63	65	43.3	48 105	ASA-4a ASA-4b
BSB-5	42.0	33.0	1.09	76	83	23.0	88	ASA-5
BSB-6	61.5	33.0	1.19	52	61	34.8	100	ASA-6
BSB-7	56.7	38.3	1.08	71	74	26.0	100	ASA-7
BSB-8	81.8	38.3	1.13	51	55		100	ASA-8
BSB-9	35.2	22.5	1.12	68	71		99	ASA-9
BSB-10	45.4	22.5	1.11	55	57		97 101	ASA-10a ASA-10b
BSB-11	98.4	87.6	1.10	90	92		99	ASA-11
BSB-12	119.9	87.6	1.10	76	79		98	ASA-12
BSN1SB-1	61.9	36.7	1.08	60	63		101	ASN1SA-1
BSN1SB-2	100.4	36.7	1.14	42	44		105	ASN1SA-2

[a] Before hydrolysis. [b] After hydrolysis.

label, and An for anthracene label. When N label is present, it is followed by a number describing the average number of vinylnaphthalene units in the chain. The letter symbols are followed by a number that refers to our laboratory protocol. For example, the symbol N4SA-1 describes the first preparation of the styrene–methacrylic acid diblock copolymer labeled at the polystyrene end by four vinylnaphthalenes. Hydrolyzed samples carry the same laboratory number as the unhydrolyzed samples from which they were prepared.

Molecular weights of the unhydrolyzed copolymers, $\bar{M}_{GPC}$, their polydispersities, $\bar{M}_w/\bar{M}_n$, and molecular weights of their constituent polystyrene blocks, $\bar{M}_s$, were determined by GPC. All samples had a quite narrow distribution of molecular weights. The use of polystyrene calibration implies that the measured molecular weights $\bar{M}_{GPC}$ are correct for polystyrene samples, but may differ from the true molecular weight $\bar{M}_{tr}$ for the copolymers. In order to obtain an estimate of $\bar{M}_{tr}$ we assumed the validity of the universal calibration of GPC columns that for our case implied

$$\bar{M}_{GPC}[\eta]_s = \bar{M}_{tr}[\eta] \tag{1}$$

where $[\eta]$ and $[\eta]_s$ are intrinsic viscosities in the solvent employed (THF) of the actual sample and of a hypothetic polystyrene sample with molecular weight $\bar{M}_{GPC}$, respectively. From the Mark–Houwink relations for polystyrene in THF at 25 °C we have selected the relation[21]

$$[\eta]_s = 0.011\bar{M}_{GPC}^{0.725} \tag{2}$$

We have verified this relation using the standard polystyrene samples. For all our polymers, the values of $\bar{M}_{tr}$ differed less than 15% from the values of $\bar{M}_{GPC}$.

The fraction of styrene units in the unhydrolyzed copolymer, f_s, was estimated from N_{Al} and N_{Ar}, the areas in the proton NMR spectrum corresponding to aliphatic and aromatic hydrogens, respectively. (The samples were dissolved in deuterated chloroform.) The following relation for f_s may be easily obtained:

$$f_s = 14/[11 + 5N_{Al}/N_{Ar}] \tag{3}$$

The results are also presented in Tables I and II (as mol % PST = $100f_s$). Values of f_s calculated from $\bar{M}_s$ and $\bar{M}_{GPC}$ agreed with the NMR values quite satisfactorily.

The hydrolyzed copolymers are insoluble in hydrocarbon solvents, in chloroform, and in dimethyl sulfoxide. They are soluble in 1,4-dioxane, but in most cases these solutions were slightly turbid. Clear molecularly dissolved solutions were obtained in a mixture of 1,4-dioxane with 20 vol % of methanol. The proton NMR spectra were therefore measured in the mixture of 80 vol % of deuterated di-

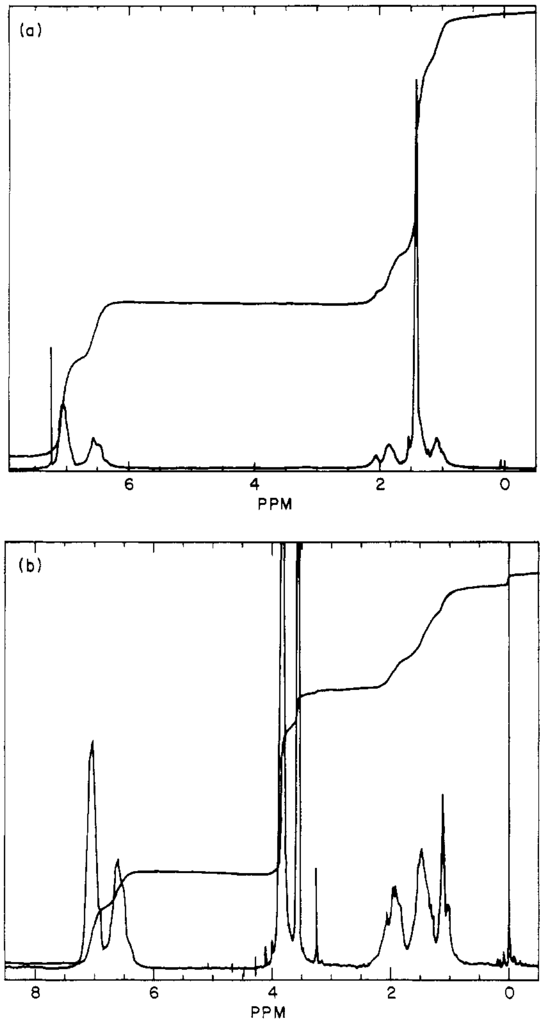

Figure 2. Proton NMR spectra (a) copolymer BSB-9 in chloroform-*d* (b) copolymer ASA-9 in 80% dioxane-*d*/20% methanol-*d*.

oxane with 20% of deuterated methanol. (The NMR spectra of unhydrolyzed copolymers in this mixture were fully equivalent to their spectra in chloroform.)

Typical spectra of unhydrolyzed and hydrolyzed polymers are presented in Figure 2. The areas H_{Al} and H_{Ar} corresponding, respectively, to aliphatic and aromatic hydrogens of the hydrolyzed samples can be combined with the values N_{Al} and N_{Ar} obtained for their unhydrolyzed parents and yield the degree of hydrolysis of the ester group, x_{hydr}, as

$$x_{hydr} = {}^{14}/_{9}\left[1 - \frac{H_{Al}/H_{Ar} - 0.6}{N_{Al}/N_{Ar} - 0.6}\right] \qquad (4)$$

Values of x_{hydr} (as calculated from eq 7) are also included in Tables I and II.

The molecular weight of several hydrolyzed copolymers was measured by static light scattering of their solutions in the dioxane/20 vol % methanol mixture. The refractive index increments required for the latter method were measured after dialyzing the solution of the copolymer against the mixed solvent.[22,23] In Table III we have collected the refractive increments of these samples $(dn/dc)_\mu$, their molecular weights $\bar{M}_w^{LS}$, and $\bar{M}_w^{h}$, the molecular weight of these copolymers that was calculated from the GPC and NMR data of the unhydrolyzed copolymers assuming that no degradation of the backbone took place during the hydrolysis. The agreement between the two sets of values of molecular weight is satisfactory.

Table III
Refractive Increments after Dialysis of Several Hydrolyzed Copolymers and Their Molecular Weights Measured by Light Scattering and Calculated from Properties of Their Unhydrolyzed Parents

sample	$(dn/dc)_\mu$	$\bar{M}_w^{LS} \times 10^{-3}$	$\bar{M}_w^{h} \times 10^{-3}$
SA-1	0.136	44	40
SA-2	0.115	64	61
SA-3	0.166	31	31
SA-5	0.155	42	38
SA-6	0.140	15	14
SA-7	0.153	115	132
SA-8	0.155	160	177

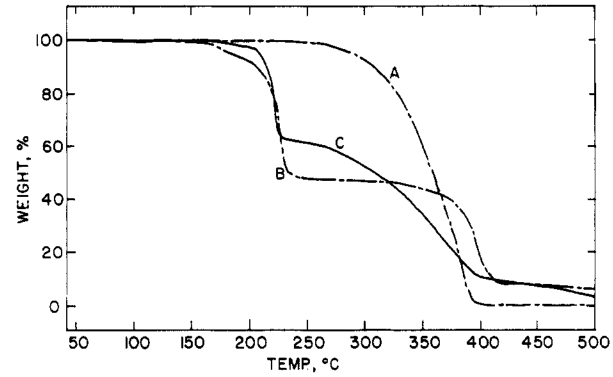

Figure 3. Thermograms for polystyrene (curve A), poly(*tert*-butyl methacrylate) (curve B), and nonhydrolyzed copolymer SB-3 (curve C).

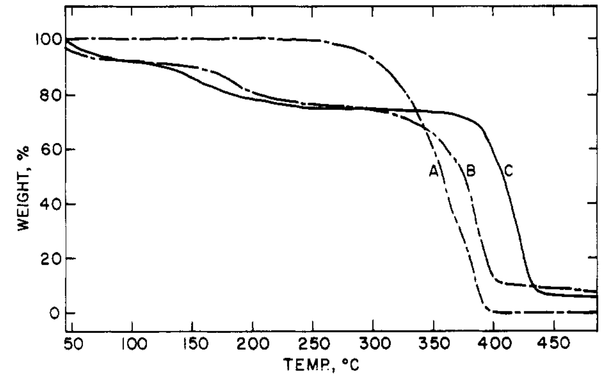

Figure 4. Thermograms for polystyrene (curve A), poly(methacrylic acid) (curve B), and hydrolyzed copolymer SA-3 (curve C).

Thermograms (TGA results) for a nonhydrolyzed copolymer, polystyrene, and poly(*tert*-butyl methacrylate) are presented in Figure 3. The decomposition of the *tert*-butyl ester group starts at about 180 °C and is completed at about 230 °C in the homopolymer and at about 210 °C in the copolymer. The polymer residue after the decomposition of the ester is quite stable up to about 360 °C. It is fully decomposed at 390 °C. The thermogram of the unhydrolyzed copolymer suggests that the blocks decompose independently.

Figure 4 presents thermograms for a hydrolyzed polymer, polystyrene, and poly(methacrylic acid). The decomposition of the poly(methacrylic acid) chains proceeds in three stages. The first stage is completed at about 100 °C and probably consists of the loss of water and the formation of anhydrides from the polyacid carboxyles. The second stage is extended to about 210 °C and probably represents loss of CO_2 and CO. The remainder of the block decomposes between 360 °C and 400 °C. It is interesting to note that homopolystyrene starts decomposing at about 270 °C and is fully decomposed at 390 °C. On the contrary, the polystyrene block of the block copolymer is stable up to 390 °C and is fully decomposed only at 430 °C.

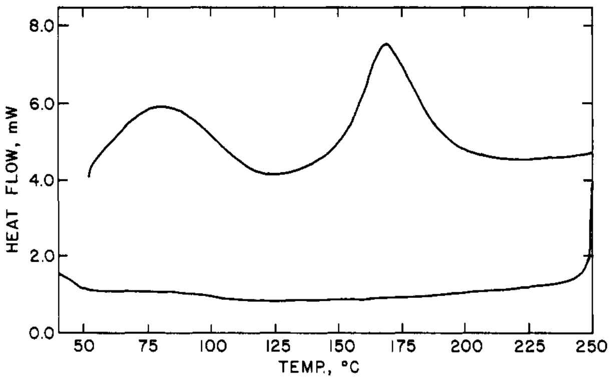

Figure 5. DSC thermogram for the hydrolyzed copolymer SA-7.

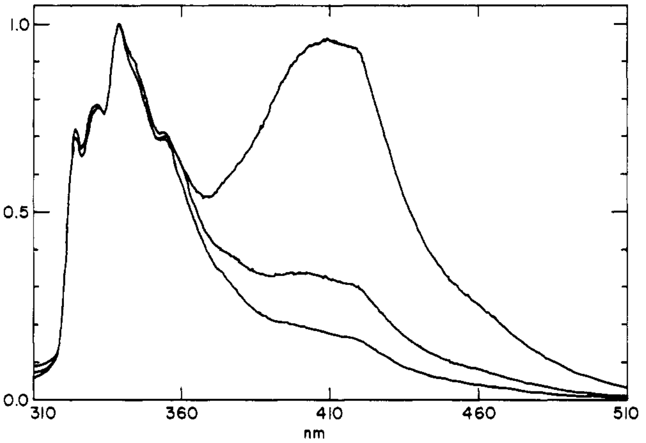

Figure 6. Fluorescence spectra of naphthalene labeled copolymers. N4SB-2, upper curve; N1SB-3, middle curve; N1SB-4, lower curve.

The DSC experiments for the unhydrolyzed sample were performed only up to 190 °C in order to avoid the polymer decomposition. In both the heating and cooling cycles a glass transition (possibly two closely separated transitions) were observed between 100 and 120 °C; they correspond to T_g's of both homopolymers.

The DSC thermograms for the hydrolyzed samples (Figure 5) exhibited during the first heating two distinct exothermal events at 90 °C and 180 °C that correspond to two decomposition temperatures observed in the TGA experiments. In the cooling period and during the second heating these events were not observed anymore; T_g was observed at about 100–110 °C.

The fluorescence-labeled copolymers were intended primarily for the study of micellar properties of our copolymers in selective solvents. Results of this study are being reported separately.[24,25] However, one set of these copolymers provided an interesting insight into the dynamics of molecular coils even in solution. Among our naphthalene-labeled copolymers, the sample N4SB-2 contained on average four naphthalene groups per chain, the sample N1SB-3 contained slightly more than one, and the sample N1SB-4 contained slightly less than one.

The fluorescence spectra of these polymers recorded in dioxane are given in Figure 6. There are two peaks in the spectrum of N4SB-2: one at 340 nm and the other at 410 nm. The peak at 340 nm is due to monomer fluorescence, and the peak at 410 nm, to excimer fluorescence. The intensities of both peaks are approximately the same, indicating that in a good solvent (dioxane), the excimer formation is fast and easy and a large fraction of excited monomers form excimer during the lifetime of excited state. This is understandable because N4SB-2 contains a block of four (on average) pendant fluorophore groups at the polystyrene end. The head-to-tail addition of vinylnaphthalene monomers enables the naphthyl moieties to adopt a coplanar "sandwich" arrangement having a proper distance between them. The excimer peaks in N1SB-3 and N1SB-4 are not so pronounced. In N1SB-3 the peak appeared as a shoulder and in N1SB-4 it was barely visible, indicating that the number of neighboring pendant fluorophore groups is quite small. This implies that the naphthalene groups from different copolymer molecules are not aggregated, at least on the time scale of the lifetime of the excitation. The excitation spectra of these copolymers are essentially identical to that of methylnaphthalene.

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